PB 168 795

ENVIRONMENTAL HEALTH SERIES
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EVALUATION OF THE USE OF ACTIVATED CARBONS AND CHEMICAL REGENERANTS IN TREATMENT OF WASTE WATER

AWTR-11

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Public Health Service

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EVALUATION OF THE USE OF ACTIVATED CARBONS AND CHEMICAL REGENERANTS IN TREATMENT OF WASTE WATER

R. L. Johnson, F. J. Lowes, Jr.,
R. M. Smith, and T. J. Powers

for

The Advanced Waste Treatment Research Program
Basic and Applied Sciences Branch
Robert A. Taft Sanitary Engineering Center

A report submitted in fulfillment of a contract between the Public Health Service and Dow Industrial Service. (Contract Number SAph 76290 for the period December 26, 1960 to February 28, 1961.) Submitted December 1962.

U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

Public Health Service

Division of Water Supply and Pollution Control

May 1964

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Public Health Service Publication No. 999-WP-13

ADVANCED WASTE TREATMENT RESEARCH PROGRAM

The Advanced Waste Treatment Research Program of the Public Health Service has two ultimate goals: One is to help abate our Nation's growing water pollution problems, and the other, more startling in concept, is to renovate waste water for direct and deliberate re-use.

Conventional water and waste treatment practices have little or no effect on many simple inorganic salts and permit an ever-increasing number and amount of highly complex, synthetic organic wastes to contaminate drinking water supplies. If we are to protect these water supplies for the future, it is mandatory that new technologies for water and waste treatment be developed.

Advanced Waste Treatment may be looked upon as a two-step process: (1) Separating concentrated contaminants from the purified water "product," and (2) disposing of the concentrated contaminants in a way that will render them forever innocuous. This "permanent disposal" of separated wastes is essential so that useable surface or ground waters will not be contaminated and so that the same contaminants need not be removed again and again from water supplies.

In one step, then, advanced waste treatment, i.e., water renovation, could alleviate both water pollution and water supply problems – problems of increasing concern both in this country and in the rest of the world. The importance of advanced waste treatment was recognized by Congress in its 1961 amendments to the Federal Water Pollution Control Act (Public Law 87-88). This act directs the Secretary of Health, Education, and Welfare ". . . to develop and demonstrate practicable means of treating municipal sewage and other water-borne wastes to remove the maximum possible amounts of physical, chemical, and biological pollutants in order to restore and maintain the maximum amount of the Nation's water at a quality suitable for re-use."

It is too early to predict accurately the cost of advanced waste treatment technology, but the need is inevitable. Because of population increase and industrial expansion, we are approaching the time when our rivers and streams will no longer be able to assimilate our wastes and when there will be no more developable supplies of fresh water. Whatever the cost of this technology, one thing is certain – <u>it must be the very lowest science and engineering can achieve.</u> Anything more will impose an inexcusable, perhaps intolerable burden on our country's economic growth and on its ability to compete in tomorrow's world.

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ABSTRACT

The capacities of six activated carbons for the soluble organics in filtered secondary effluent were obtained by use of a continuous-flow, column-type test. Results varied from 7 to 13 grams COD per 100 grams of carbon. Because of the manner in which the test was carried out, only the carbon with the smallest capacity was loaded to the maximum extent possible.

The chemical regeneration of exhausted carbon was investigated by use of nine inorganic oxidizing agents. Only hydrogen peroxide was capable of restoring measurable adsorption capacity after more than two cycles of exhaustion and regeneration. The economic feasibility of chemical regeneration is not promising.

EVALUATION OF THE USE OF ACTIVATED CARBONS AND CHEMICAL REGENERANTS IN TREATMENT OF WASTE WATER

Introduction

Current water shortages and the prospect of more have prompted investigations into sources of potable water other than those represented by fresh-water supplies from lakes, streams, and underground. Present municipal use of fresh water is estimated at 150 gallons per capita per day while only 30 years ago this figure was 100 to 120 gallons per capita per day. This growth in municipal use plus an increase in population and the tremendous increase also expected in industrial usage make it evident that our water requirements of the future are certain to be much greater than those of the present. This growth in water requirements must be faced with the knowledge that our fresh-water supply is a relatively fixed amount. In view of these stark predictions, it becomes almost imperative to use our available water over and over again. Re-use of water by industry is presently practiced in several sections of the country. Chanute, Kansas, for example, re-used waste water after treatments during a 5-month drought in the winter of 1956; Lyndon, Kansas, re-used waste water during the fall of 1956.[6]

Unfortunately, with every re-use of water, contaminants are added that resist conventional processing. These are called "refractory" contaminants. Pollution of natural waters by these refractory materials has attained a certain scientific and public notoriety. The ever-increasing industrial expansion in plastics, dyes, organic chemicals, insecticides, fertilizers, and synthetic fibers has obviously been responsible for many of these pollutants.

The effect of many of these contaminants in respect to the re-use of water is not known. Fish kills that result from pollution of natural waters are, of course, well known and highly publicized. Foaming of natural water, resulting from contamination with surfactants, has also received much publicity. The effects of many other refractory materials, especially over long periods of time, are not known. Tolerance levels

have not been established for many of the compounds that can reach surface waters. For example, of over 500,000 synthesized organic chemicals, only several dozen have been determined safe by the Food and Drug Administration for addition to foods.[13] Many of these refractory materials give no indication of their presence and many cannot be completely removed from water supplies or waste waters by conventional waste treatment methods.[6, 13, 19, 23, 24, 25] Hurwitz, et al.[19] have followed the assimilation of alkylbenzenesulfonate (ABS) in receiving streams and found a very slow and incomplete removal by natural waters. Culp and Stoltenberg[10] have reported synthetic-detergent concentrations in the Marais des Cygnes River as great as 6.6 milligrams per liter below the waste-water treatment plant outfall at Ottawa, Kansas. Although records indicate no human illness associated with organic chemical pollution in the past, this is no guarantee that there will be none in the future.

According to Middleton,[28] many different kinds and quantities of synthetic organic chemicals are being detected in both raw and treated water. He further states that repeated exposures over long periods of time to even small concentrations of these materials may represent a public health threat of major proportions. Usually, the first recognized indication of pollution is the development of tastes and odors in treated water, but many of the compounds that produce these tastes and odors have not been identified except in broad classifications. Middleton et al.[26, 27] and others,[7, 32, 33] by using activated carbon, have attempted to identify these compounds and other organics present in surface and treated waters. Phenolic, antibiotic, sugar beet, distillery, slaughterhouse, and pulp and paper wastes are known sources of some tastes and odors.[2]

Activated carbon has been used since 1927 for removal of tastes and odors in water.[3] It is usually applied, in a water slurry, at a rate of from 20 to 40 pounds per million gallons, though doses have varied from 2 to 1,800 pounds per million gallons.[34] Harrison[15, 16] has described in some length the installation and operation of the Bay City, Michigan, water plant where powdered carbon slurries are used. Recent work by Vaughn et al.,[37] Lieber,[20] and Renn and Barada[31] has shown that synthetic detergents can be removed from waste water and raw water by the use of activated carbon. A carbon dosage of 240 milligrams per liter has removed 97 percent of a 20-milligrams-per-liter synthetic-detergent concentration from raw water.[37]

Complete descriptions of the use of activated carbon in water treatment for the removal of tastes and odors are available.[2, 9, 17] Eckenfelder[12] recently showed that activated carbon could be used to remove detergents satisfactorily from a public automatic-laundry waste.

The preparation of activated carbon involves two basic procedures, char formation and activation. In some cases, both operations are done in one step while in others the char is transported and activated in a separate reaction. Char formation is accomplished with hardwood by heating and drying it to decrease its weight by 15 to 20 percent through water loss. Activation is then carried out by slowly increasing the temperature to 250°C where it is held until tars distill off. Finally, the temperature is increased to 400°C, and calcium, magnesium, or zinc chloride are added. Carbonization will take place in a temperature range of 400 to 900°C within which activated carbon is produced.

The removal of organic materials from water and waste water by activated carbon is accomplished by adsorption.[4, 8, 18, 22] Many other adsorbents are commercially available but have had limited application in this field.

In water treatment for the removal of tastes and odors, powdered, activated carbon is almost universally used. In this type of treatment the carbon is used only once and then discarded. Where powdered-carbon dosages would be prohibitive in cost, granular, activated carbon may be used. Granular carbon is used until it becomes exhausted, and then it is regenerated. Regeneration can be accomplished by the elution of the adsorbed material by a suitable solvent, by heating, or by other chemical means.[18, 35, 37]

When activated carbon is used for the removal of free chlorine, after excess chlorination, it is used as a reducing agent as well as adsorbent.[5] The free chlorine is converted to chloride ion. The behavior of various oxidizing agents with activated carbon has been determined by Behrman and Gustafson.[5] The carbon reacts in one of three ways:

1. It adsorbs and decomposes the oxidizing agent;

2. it adsorbs the oxidizer, which reacts with the carbon;

3. it adsorbs the oxidizer with no reaction of either the carbon or oxidizer.

No published data have been found concerning the specific use of activated carbon in waste-water treatment for removal of soluble organic matter. Consequently, there is a lack of publications on chemical oxidation regeneration of activated carbon exhausted by waste water.

The investigations described here have three objectives:

1. Determine the capacity of carbon to adsorb materials from a municipal waste water that has been subjected previously to conventional methods through the secondary-treatment process.

2. Determine if commercially available chemical oxidants can regenerate an activated carbon that has exhaustively adsorbed soluble municipal-waste materials.

3. Describe some of the conditions necessary for optimum performance of the best chemical oxidant resulting from a regeneration of exhausted, activated carbon.

PHASE 1.

STUDIES ON WASTE-WATER ADSORPTION BY ACTIVATED CARBON

The purpose of this phase of the project was to determine the capacity of activated carbon to adsorb soluble materials from wastes previously subjected to conventional treatments. If feasible, comparative evaluations of several activated carbons would be made to select a single carbon for further experimentation.

Experimental Procedures

MATERIALS AND EQUIPMENT

Source of Conventionally Treated Waste Water

The Midland Waste-Water Plant serves the City of Midland, Michigan, and treats approximately 15 percent of the domestic waste water of The Dow Chemical Company. The daily flow rate ranges from 2.1 to 3.5 million gallons. These figures are based on the average daily flow and do not include ultimate high or low figures. Waste water gets only primary treatment here. The suspended solids coming into the plant average, during a year (1961), 171 milligrams per liter as calculated on daily samplings. The suspended solids as effluent from the plant to the Tittabawasee River average 77 milligrams per liter. The BOD average of the raw-waste-water influent to the plant is 178 milligrams per liter; the effluent BOD to the river, 103.

Pilot Plant for Producing Activated-Carbon Feed

Since the plant utilizes only primary waste-water treatment, an activated-sludge pilot plant model was fabricated to obtain secondary effluent. It was designed to simulate the normal behavior of large-scale, conventional treatment processes. Operation was controlled so that the analytical data obtained would compare favorably with the results of a full-scale secondary-treatment plant. Careful adjustments of air, influent flow (primary effluent), and sludge wasting were maintained to produce adequate oxygenation, flocculation, and COD removal for the batch collection of treated secondary waste. To provide such a waste, a small, activated-sludge-settling tank unit of 6.5-gallon capacity was constructed by following the design of Ludzack's unit as used at the Taft Center.[21] This unit was operated at a flow rate of 60 to 70 milliliters per minute and was supplied 15 psi compressed air, at the rate of 2 to 2.5 liters per minute.

At this hydraulic rate, minimum detention time in the unit was about 6.5 hours, with approximately 5.25 hours in the aeration zone. In view of the strictly domestic nature and comparative weakness of Midland waste water, this detention time should produce a stable effluent. The mixed-liquor suspended solids were maintained at about 1,000 milligrams per liter by daily wasting of mixed liquor.

The activated sludge was produced by operating the unit at full capacity on primary-waste-water effluent for several weeks. Analyses of suspended solids were made sufficiently often to determine the increasing mixed-liquor suspended solids. Performance data of the unit are listed in Table 1.

Table 1. PERFORMANCE DATA FOR PILOT SCALE ACTIVATED-SLUDGE UNIT

Days operation	Suspended solids, mg/liter
0	27.5
1	289
3	165
4	150
5	105
8	316
10	595
11	270
12	410
15	620
17	1,100

After 17 days of operation, the activated-sludge unit stabilized satisfactorily and operated without problems throughout the experimental program. This pilot scale, secondary-waste-water treatment system was further supplemented by a tertiary filter, consisting of graded gravel and one layer of very fine sand, and finally of glass wool.

Approximately 70 percent removal of COD from raw waste water was accomplished by passage through the Midland primary-treatment plant, activated-sludge pilot plant unit, and tertiary filter. The remaining 30 percent COD provided the source of polluted influent for the activated-carbon experiments.

The tertiary-treated waste water was collected and stored in a 40-gallon drum. In a 48-hour period, an ample supply of tertiary waste water was made available for a thorough study of the adsorptive properties of a carbon type. Figure 1 illustrates diagrammatically the waste treatment system utilized throughout the program.

Pumping Equipment

Piston pumps, manufactured by A & F Machine Products Company, were used to pump the tertiary-effluent waste water through the activated-carbon columns. Multiple heads on these

pumps permitted the comparative evaluation of as many as six activated-carbon columns during one exhaustion experiment. The flow rates of these pumps could be accurately regulated for a flow of from 10 to more than 100 milliliters per minute.

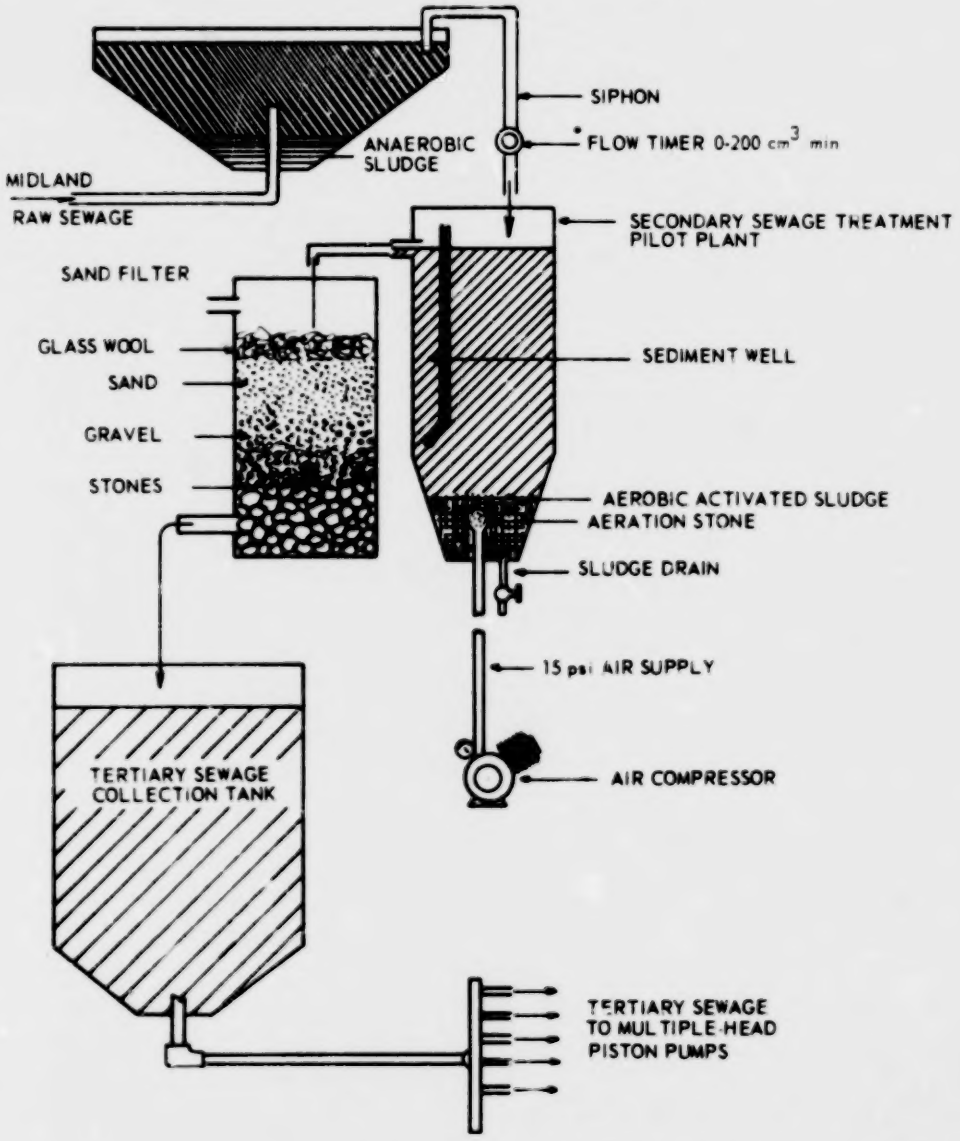

Figure 1. Midland sewage treatment plant and pilot plant unit.

Activated Carbons

The following commercially available, activated carbons were selected for potential adsorptive abilities to remove COD from tertiary waste water:

Activated-carbon identity	Mesh size	Manufacturer
Pittsburgh	8 x 30	Pittsburgh Chemical Company
Barnebey Cheney	8 x 12	Barnebey Cheney Company
Cliffs Dow	10 x 30	Cliffs Dow Chemical Company
Atlas	12 x 20	Atlas Chemical Company
American Norit	8 x 20	R. W. Greeff & Co., Inc.
West Virginia	C-190 x 30	W. Virginia Pulp & Paper Co.

METHODS

Evaluation of Commercially Available, Activated Carbons

Although it is well known that activated carbon can adsorb many organic materials from aqueous solutions, experimental work to determine the adsorptive capacity of activated carbon for the soluble organics present in secondary-treatment plant effluents has not been performed or at least has not been reported in the literature. It was necessary, therefore, to evaluate the various carbons for their adsorptive capacity on these materials.

At the time of the writing of this contract, it was stipulated that all work on the carbons would be carried out on an actual effluent from a secondary-treatment plant. This posed many problems owing to the extreme variability of such a waste stream. By taking this variability into account, it was concluded that at least a composite, of 24 hours' duration, would have to be used for the studies of adsorptive capacity. Moreover, since most individual constituents in such a stream are present only in minute amounts, only a general determination of organic matter could be utilized for evaluating the capacity. Such a test is the COD (Chemical Oxygen Demand). The sensitive modification, for dilute samples, was used throughout this study.

Initial studies were made to determine the adsorptive capacity of the previously mentioned carbons for the soluble organics in the tertiary-waste-water effluent (sand-filtered, pilot plant effluent). By adsorptive capacity is meant the percent, by weight, of the carbon's weight that it could adsorb without exhaustion. These studies were made with 1-inch-diameter columns.

The use of columns was based on the phenomenon that an organic "front" moves downward through a bed and that total exhaustion is not accomplished until the total bed has had this "front" pass through it. The use of batch systems was con-

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sidered for this phase of the evaluation. The carbon would then, however, be only in equilibrium with the organic constituents in the waste, while still having adsorptive capacity remaining. It is also quite difficult, if not impossible, to scale up to column conditions from batch observations. Since this entire study was geared to conditions that would approximate actual field operation, it was felt that this was a valid decision.

The columns used for this phase of study were 100-millimeter burets. The carbon, generally 15 grams, was placed in the buret on a bed of glass beads, and the feed was percolated downward through this column. The feed rate was 30 cubic centimeters per minute, which amounts to 30 to 60 bed volumes per hour based on carbon density. Grab samples of feed and effluent were taken at frequent intervals (15 to 60 minutes) for the first 4 hours and approximately once every 8 hours thereafter until the study was completed. The flow that occurred between the sampling periods was recorded. A study was terminated when the influent and effluent COD were within 5 milligrams per liter of each other, or when 180 liters of waste had been passed through the bed.

It is common knowledge that the organic content of waste water varies hour by hour; hence, the composition of effluent from a plant treating waste water would also vary. For instance, the chloride concentration would vary when thawing snow would carry salt into the combined sewer system; ABS would be high on certain days; COD would be high about 1:00 p.m. and lowest about 3:00 a.m.

It was felt that we could eliminate much of this variability if we used composited effluent as feed. This was the reason for collecting effluent to use for this study rather than accept the actual tertiary effluent on a continuous basis from the unit. A definite problem that arose later as a result of this decision was the gradual degradation of the influent COD concentration owing to biological action in the stored waste. This degradation was accelerated as the waste was stored at room temperature. It was obvious that sand filtration had not eliminated the microorganisms that caused this COD reduction. A solution to this problem in future studies would be the pasteurization or sterilization of the waste prior to storage. This degradation amounted to as much as 40 percent of the original COD when the waste was stored for a period of 4 days in the laboratory. We did not determine what fraction of the COD was being degraded, nor what effect the lack of these materials during the later stages of an individual test had on the carbon's capacity or adsorption pattern.

The degradation was accounted for in computation of the adsorptive capacity of the carbons. The influent and effluent COD's were plotted, as shown in Figures 2 through 7, and the area between the curves was computed. Since one test, that on Barnebey Cheney KC-5, was run for only 143 liters, the relative adsorptive capacities for all the carbons were computed at a total flow of 140 liters. The adsorptive capacity was determined by dividing the area between the curves by the weight of carbon used for the test. Note that carbons were not of uniform size, and this may have affected adsorption capacity.

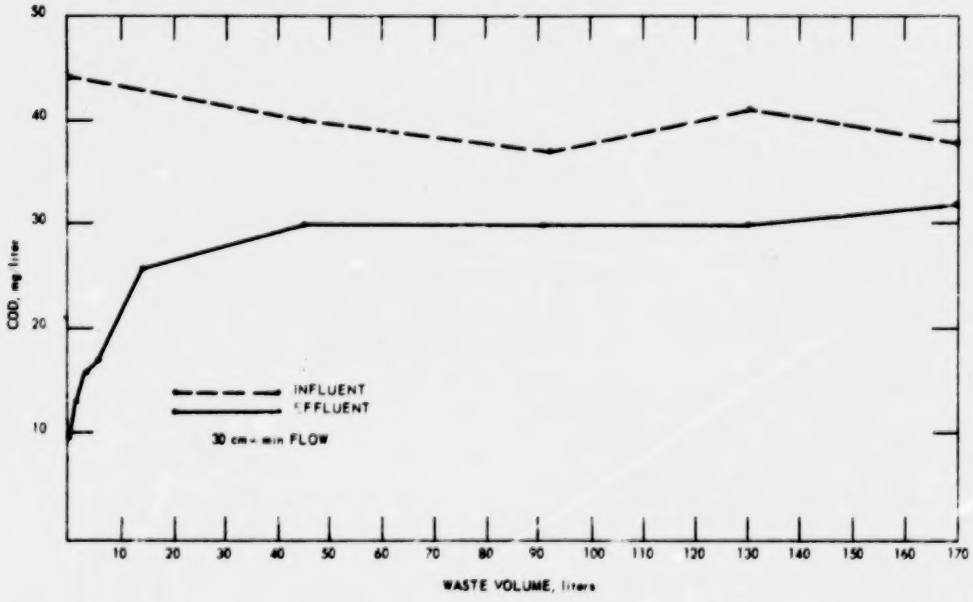

Figure 2. Pittsburgh 8 x 30 mesh, $\frac{1,575}{15,000}$ = 10.5% by weight adsorbed COD.

As a precautionary measure, possible COD residues in each batch of new, activated carbon were determined. Since manufacturing processes could possibly leave organic fragments, the interference was of concern. High-purity distilled water was percolated through activated-carbon samples, collected, and analyzed for chlorides and COD. In no case was a measurable COD found; chlorides were less than 10 milligrams per liter in the first liter of wash water and absent thereafter. The background interference was, therefore, considered insignificant.

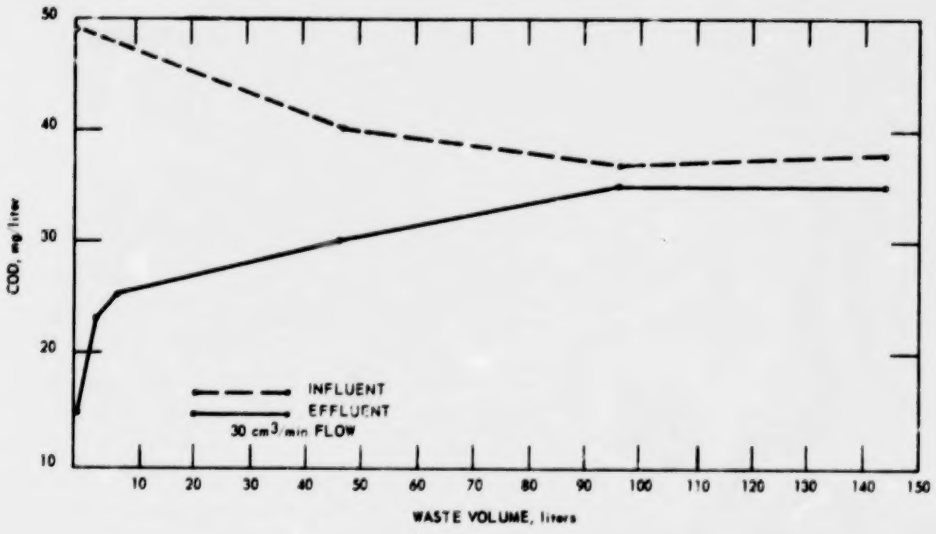

Figure 3. Barnebey Cheney KC-5, $\frac{1,215}{15,000}$ = 8.1%.

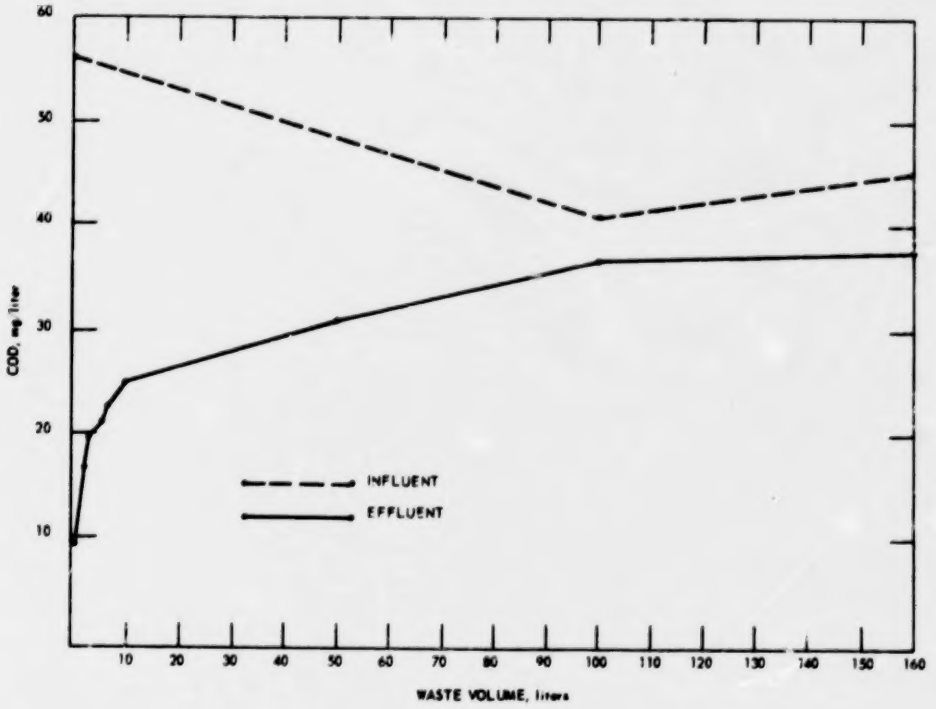

Figure 4. Cliffs Dow 10 x 30 mesh, $\frac{2,010}{15,000}$ = 13.4%.

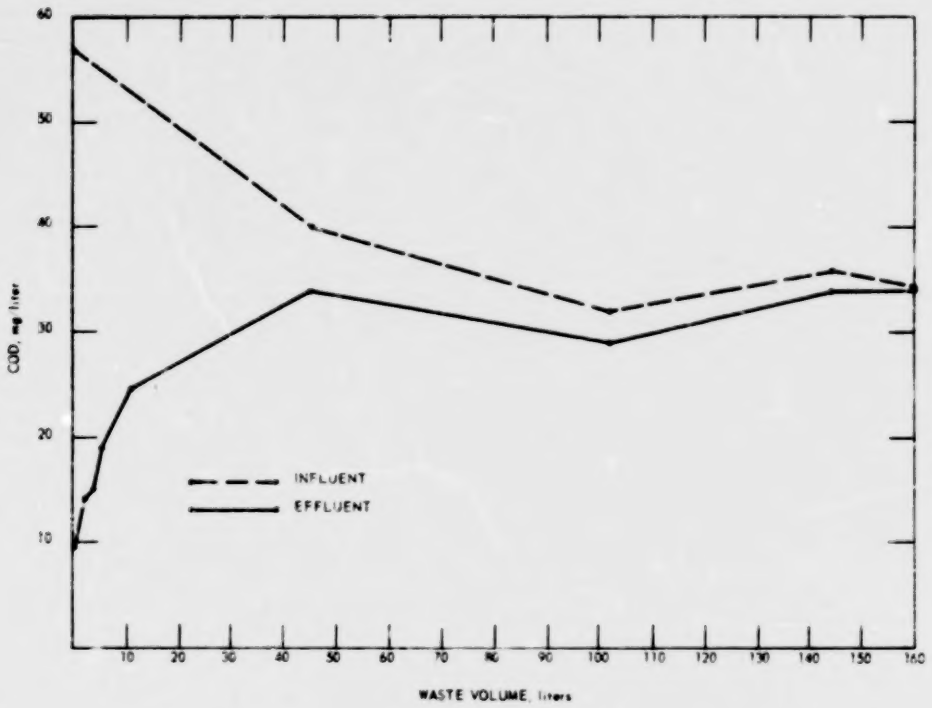

Figure 5. Atlas 12 x 20 mesh, $\frac{1,305}{15,000} = 8.7\%$.

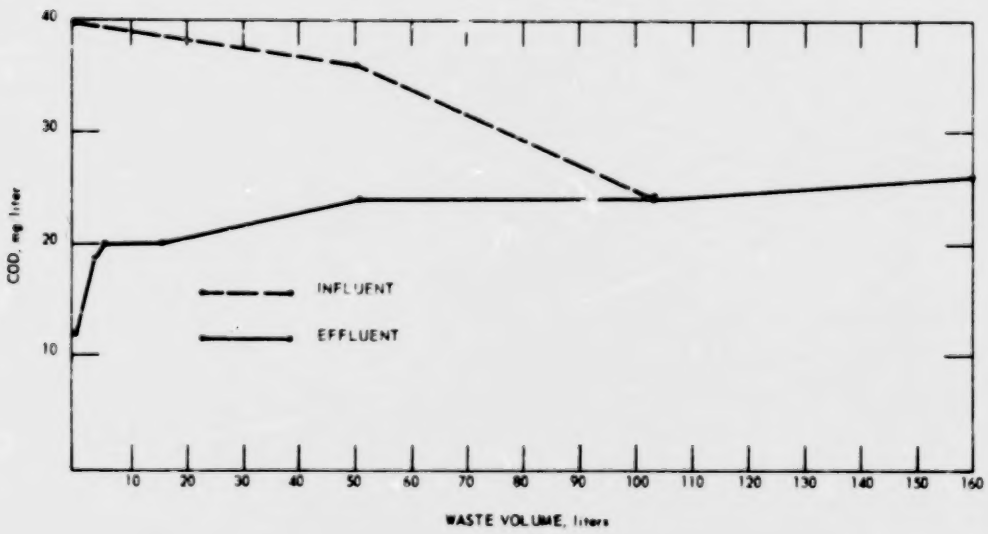

Figure 6. American Norit 8 x 20 mesh, $\frac{1,050}{15,000} = 7.0\%$.

Analytical Techniques

Chlorides

Chlorides were run by using the Mohr technique as outlined on page 78 of Standard Methods [38] with the modification of using 0.1 normal $AgNO_3$ rather than 0.0141. This was considered sufficient for this work since the only reason for running chlorides was to correct the COD data for their presence. With this normality, 0.1 milliliter is equivalent to 0.35 milligram of Cl^- per liter, or to only 0.07 milligram of COD per liter (with 0.23 x Cl^- equivalent to 1 milligram of COD per liter). No greater accuracy was required owing to limitations of the COD test used.

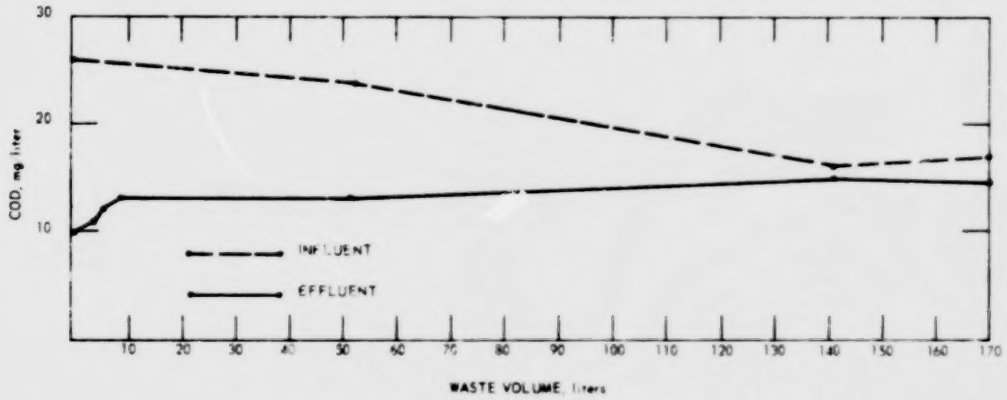

Figure 7. West Virginia C-190 x 30 mesh, $\frac{1,111}{10,000} = 11.1\%$.

Chemical oxygen demand

Chemical oxygen demand was determined by the dichromate reflux method as described on pages 399-402 in Standard Methods. The modification for dilute samples, outlined on page 402, was used. Silver sulfate was not used as a catalyst because comparative studies, with and without this agent, did not show appreciable variation in final values.

Alkylbenzenesulfonate

ABS was run in accordance with the proposed method found on page 245 in Standard Methods. This method is for use in water supplies but is considered sufficiently accurate for use in these tests. Neither the error due to the presence of chlo-

rides nor the possible errors due to other interferences were investigated.

Suspended solids

Suspended matter was determined by filtration through asbestos mat by vacuum in a Gooch crucible. Suspended solids on both activated sludge and tertiary waste water were run by this method as outlined on page 327 in the Eleventh Edition of Standard Methods. Results were recorded as total milligrams of suspended matter per liter.

Results

Figures 2 through 7 illustrate the change in influent and effluent with time for each of the activated carbons evaluated. The area between the two curves represents the amount of COD retained by the carbon.

The percent by weight of the adsorbed COD after 140 liters of tertiary effluent has been treated was calculated, and the data are shown in Table 2.

Table 2. PERCENT BY WEIGHT OF ADSORBED COD

Carbon identity	Wt % adsorbed COD	From Figure
Pittsburgh 8 x 30 mesh	10.5	2
Barnebey Cheney 8 x 12	8.1	3
Cliffs Dow 10 x 30 mesh	13.4	4
Atlas 12 x 20 mesh	8.7	5
American Norit 8 x 20 mesh	7.0	6
West Virginia C-190 + 30	11.1	7

Discussion

Liquid-phase adsorption data obtained from different sources seldom correlate because of the effect of the variable medium enhancing the natural differences in carbon activity.[18] Furthermore, the relative adsorption of different materials is not the same at all concentrations, and correlation among concentrations used by various investigators becomes difficult. In general, it has been found that the higher molecular-weight materials are adsorbed more effectively on activated carbon than are those of lower molecular weight.

Much of the adsorptive power of activated carbon has been attributed to crystal formation within the substrate. For instance, diamond powder adsorbs methylene blue but not succinic acid, while graphite adsorbs succinic acid but not methylene blue.[29] Activated carbon, however, adsorbs both succinic acid and methylene blue, and from this, it has been inferred that both crystal types are present in the active carbon. In general, it has been found that a single solute is more easily removed from a solution than are several materials in the same solvent.[1, 11, 14, 30] Other work has shown considerable preferential adsorption of one of the materials from a solution.

There are no valid theories that allow selection of the best active carbon in any single case without experimentation. Most of the materials now marketed have been the result of continued improvement for a particular job. In sugar production, one material is used to decolorize beet sugar while a different one is used for cane sugar, and yet both remove color from essentially an aqueous, sucrose solution. Most activated-carbon manufacturers, therefore, offer their products in reference to a specific demand. In some cases as many as 50 carbons from one manufacturer are sold with each available in several mesh sizes.

No attempt was made to obtain the most superior activated carbon for adsorption of refractory contaminants from Midland, Michigan, tertiary waste. The main objective was to determine the extent to which activated carbon could adsorb those contaminants that demonstrated COD values in the tertiary waste. All activated carbons evaluated showed measurable adsorptive capacities for COD materials.

The compilation of calculated-percent-adsorbed COD by weight for the various carbons evaluated (Table 2) should not be construed as valid for comparative purposes. These data were accumulated at various times, for example. Hence, there were undoubtedly differences in the degree and nature of the refractory contaminants in the waste water. In turn, these differences would affect the point at which equilibrium between the carbon adsorptive capacity and total COD in the waste would exist. The results listed should, therefore, serve only as a possible indication of differences among activated carbons in waste removal efficiency.

Cliffs Dow activated carbon was selected for use in the second phase of the project. This decision was induced solely by the ease of procurement of necessary quantities of the activated carbon selected.

PHASE 2.

REGENERATION STUDIES

The purpose of this series of experiments was to screen commercially available chemical oxidants for their ability to regenerate activated carbon partially exhausted by passage of a sand-filtered, activated-sludge effluent through carbon columns.

Experimental Procedures

MATERIALS AND EQUIPMENT

Activated Carbon

Cliffs Dow 10 x 30-mesh activated carbon was used for the screening of oxidative regenerants. This particular carbon appeared to have adsorptive capacities for components of the utilized tertiary waste water that were sufficiently great to permit comparative oxidant screening.

Regenerant Application Apparatus

The equipment required to feed the chemical oxidant to the exhausted, activated carbon is shown in Figure 8. Essentially, the apparatus consisted of a reservoir for oxidant solutions and a pumping apparatus to force the oxidant solution up through the exhausted carbon column.

Evaluation of Chemical Oxidants

Chemical oxidants evaluated as regenerants for the exhausted, activated carbon were as follows: Chlorine, bromine, potassium permanganate, sodium dichromate, sodium persulfate, potassium persulfate, sodium peroxide, hydrogen peroxide, and ozone.

METHODS

Activated-Carbon Exhaustion

To expedite the screening of oxidative regenerants, it was felt necessary to alter the procedure for exhaustion of the

activated carbon. The dynamic status of the collected tertiary-treated waste water in respect to time further prompted a change in the technique. The flow of tertiary-treated waste water through

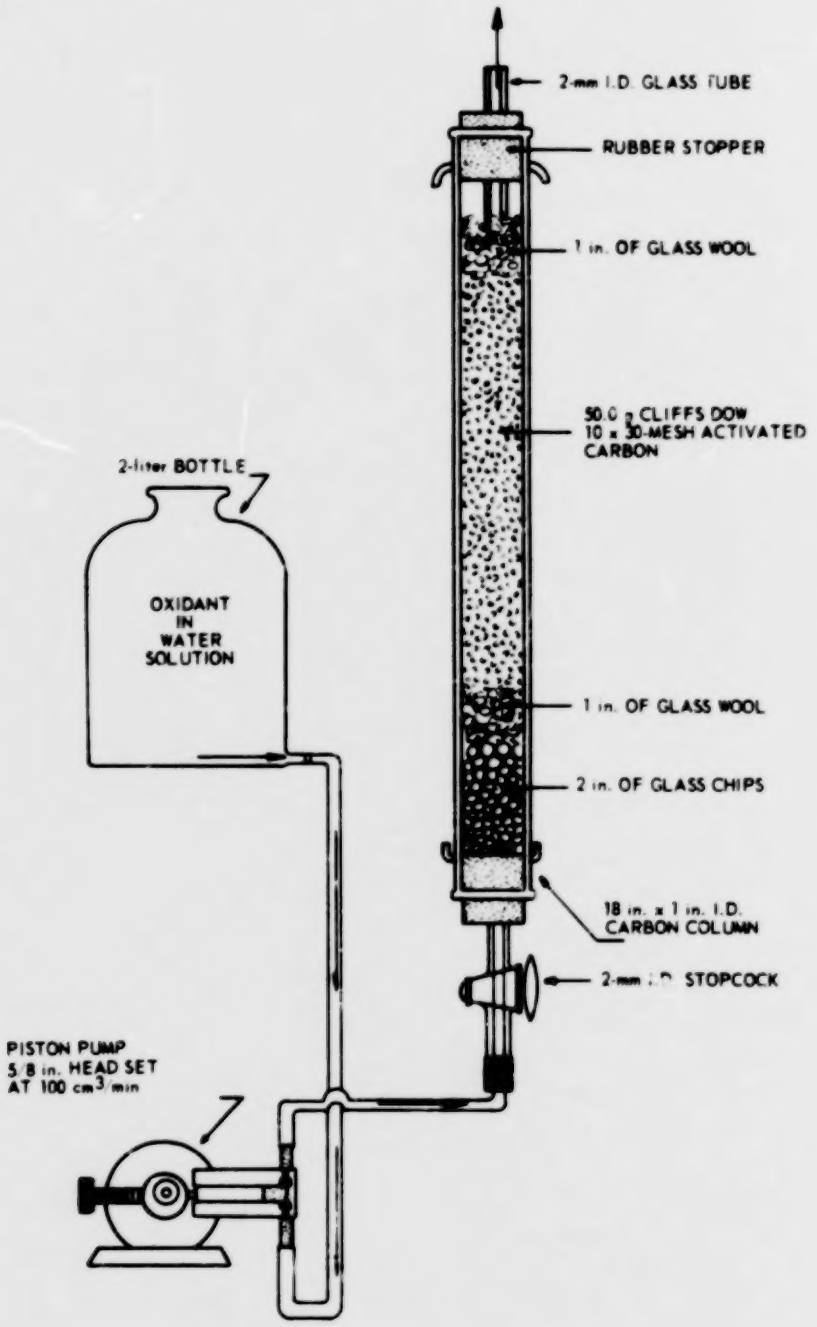

Figure 8. Carbon column with packing and regeneration application.

the activated-carbon column was increased from 30 to 100 cubic centimeters per minute. The amount of carbon exposed was also

increased from 15 to 50 grams. Several runs following these changes substantiated the belief that satisfactory exhaustion of the activated carbon could be achieved within the confines of an 8-hour working day. More efficient planning of experiments as well as more rapid data accumulation were realized by these changes.

If other factors are ignored, these changes in rate of flow and amount of carbon exposed altered the calculated percent COD adsorbed. A 25 percent increase was noted. By using area integration calculations to obtain an average efficiency value, the slower flow rate through 15 grams of carbon gave 52 percent COD adsorbed. The increased flow rate of 100 cubic centimeters per minute through 50 grams of carbon gave 77 percent COD adsorbed.

Differences in the tertiary waste water in respect to time, variations in the procedures of exhausting the carbon, and even changes in personnel would all affect these calculations. The 25 percent increase is, therefore, only approximate, but does indicate that flow rate and amount of carbon especially will affect the adsorptive efficiency of carbon exposed to tertiary waste water. This point was not pursued further.

Preparation of Oxidant Feed Stocks

No routine procedure of preparation or concentration of the various chemical oxidants could be established. Differing solubilities, stability, and source of supply all dictated that each oxidant had to be considered individually. For example, sodium dichromate is very soluble in water, and ozone is, of course, an extremely unstable gas. In general, a "reasonable" concentration was selected that would be expected to have some oxidative effect on the materials adsorbed on the carbon.

Analytical Procedures

The unstable and reactive nature of many of the oxidants was well known. Since, however, the objective was to compare oxidants for contemplated use as regenerants of exhausted carbon under practical conditions, no attempt was made to control the variables that may affect the oxidant efficiency. Only the constants of carbon amount and influent flow rate were controlled. Different conditions of exposure of exhausted carbon to the oxidants could, therefore, significantly alter the results. It should also be remembered that the carbon was exhausted by a municipal waste over which no control of variability was possible.

In spite of an awareness of these variables a comparative consideration of the regenerative efficiencies of the candidate oxidants was desirable. The method used consisted of analyses of the tertiary-waste-water COD removed by a virgin carbon sample as compared with the COD removed from the same tertiary waste water by the "regenerated" carbon. In these experiments a regenerated carbon is identified as a 50-gram amount of Cliffs Dow activated carbon that had previously been exhausted by Midland tertiary waste water and then subjected to oxidant exposure by the method previously described.

To make realistic comparisons of the regenerative efficiencies of the oxidants, a standardized sampling procedure was necessary. At a flow rate of 100 cubic centimeters per minute, a total of 42 liters of tertiary-waste-water feed could be passed through the carbon columns within the practical confines of a working day. Grab samples of the feed and column effluents were obtained at the first liter of throughput and at each sixth liter thereafter. The exception was the sampling at the 42d liter.

The regenerative efficiencies of the oxidants were determined in percent by integrated area calculations. At any sampling point the efficiency percentile could be calculated as follows:

$$Ei = \frac{Xi - Zi}{Xi - Yi} \times 100 \qquad (1)$$

where E = oxidant efficiency
X = COD of influent
Z = COD of regenerated-carbon effluent
Y = COD of virgin-carbon effluent, and
i = any sampling point.

The efficiency values can then be fitted into the following integrated area formula:

$$\text{Avg regenerant \% efficiency } (E_o) = \frac{3E_1 + 6(E_2 + E_3 -- + E_6) + 5.5E_7 + 2.5E_8}{41} \qquad (2)$$

where E_1 = Ei at 1 liter throughput
E_2 = Ei at 7 liters throughput
E_3 = E_2 + 6 liters throughput, etc.
E_8 = E_7 + 5 liters throughput.

In Table 3, for example, COD values and efficiency calculations were determined for chlorine water.

Table 3. COD VALUES AND EFFICIENCY CALCULATIONS FOR CHLORINE WATER

Throughput, liters	COD removed by virgin carbon, ppm	COD removed by regenerated carbon, ppm	Regenerative efficiency, %
1 (E_1)	45	9	20
7 (E_2)	44	7	16
13 (E_3)	38	8	21
19 (E_4)	32	6	19
25 (E_5)	32	6	19
31 (E_6)	26	2	8
37 (E_7)	25	2	8
42 (E_8)	22	2	9

The derived percent efficiency determinations were than inserted into the integrated area formula to obtain the average regenerative efficiency as follows:

$$\frac{3(20) + 6(16 + 21 + 16 + 19 + 8) + 5.5(8) + 2.5(9)}{41} = 14.7\%$$

With the exception of bromine water, all the oxidants evaluated were compared on the basis of the efficiency calculations.

Results

The results of the screening of oxidants for regeneration of exhausted carbon are based on a minimum of four replications. Two-liter volumes of each oxidant were fed at a flow rate of 100 cubic centimeters per minute. It also became obvious, as this phase of the project progressed, that a single exhaustion-regeneration step or cycle was not significant. Further differentiation of the oxidants was achieved by second and third exhaustion-regeneration cycles. For convenience in reporting the results, ERC will denote "exhaustion-regeneration cycle." The oxidants screened and the results obtained are as follows:

1. Chlorine. This oxidant was prepared for regeneration evaluation as a saturated water solution. The concentration of active chlorine was approximately 4,600 ppm, and the percentage recovery of activated-carbon

adsorptive capacity induced by chlorine was considered to be very poor. The regeneration, based on the average of 11 single ERC determinations, was calculated to only 15 percent recovery.

2. Bromine. A saturated (approximately 0.35%) solution of bromine was fed through exhausted carbon columns. The apparent adsorption of bromine on the carbon caused gross errors in the COD analyses of the grab samples of carbon effluent. Approximately 25 liters of wash water (or tertiary-treate waste) was required to rid the carbon completely of bromine. Consequently, no worthwhile data were obtained on the efficiency of bromine as a regenerant for waste-exhausted, activated carbon. The meager results that were accumulated indicate that bromine is no more efficient than chlorine.

3. Potassium permanganate. The high water solubility of $KMnO_4$ prompted the arbitrary selection of a 10 percent solution of this oxidizing agent. The recovery of adsorptive capacity by the carbon averaged 16 percent for a single ERC. Potassium permanganate also discolored all components of the apparatus. The low recovery plus the staining discouraged further investigations with this oxidant.

4. Sodium dichromate. The percent recovery of adsorptive capacity by the carbon on the first ERC with $Na_2Cr_2O_7$ was superior to those obtained with any of the previous oxidants. Sixty percent recovery was demonstrated on the first ERC. The recovery dropped off grossly on the second ERC; only 15 to 20 percent recovery was evident. No measurable regeneration was observed on the third ERC.

   It was also noted that the characteristically yellow color of Cr_2O_7 showed that this chemical had an affinity for the carbon. The dichromate was difficult to remove and showed up in the column effluent during a second ERC even after the passage of 20 liters of treated waste water.

5. Potassium persulfate. The results obtained with $K_2S_2O_8$ pointed out that the average recovery of adsorptive capacity by the carbon on the first ERC was 49 percent. Data on second ERC experiments showed a drop of regenerative restoration to 20 percent. Nevertheless, $K_2S_2O_8$ provided the best regeneration

so far when the carbon was subjected to a second ERC. Unfortunately, no regeneration of the carbon was apparent on the third ERC.

6. Sodium persulfate. Essentially equivalent to $K_2S_2O_8$ on the initial ERC (55%), $Na_2S_2O_8$ was much less efficient in regenerative ability on the second ERC. The average recovery on a second ERC was less than 20 percent.

7. Sodium peroxide. This chemical was selected for evaluation because, in addition to its well-known oxidizing properties, it had a sodium ion available. An interesting theory was considered that a possible saponification of adsorbed fatty acids could occur in conjunction with the oxidizing effect.

   Sodium peroxide gave favorable results on the first ERC. The recovery of adsorptive capacity was calculated to be 60 percent. This promising recovery rate decreased, however, to less than 20 percent on the second ERC and to an unmeasurable percentile on the third ERC.

8. Ozone. The instability of ozone necessitated generation of the gas and immediate feed into the exhausted carbon column. The amount of ozone was governed by the generating apparatus and the time of exposure. The amount of molecular ozone fed to the 50 grams of carbon was 2.5 grams.

   The carbon-regenerating capacity of ozone was demonstrated to be very limited. The first ERC resulted in only 25 percent recovery.

9. Hydrogen peroxide. Regeneration of exhausted, activated carbon with hydrogen peroxide was done initially with a 30 percent aqueous solution. This experiment was carried out in an explosion-proof hood because of the danger involved in combining concentrated H_2O_2 with organic matter. This form of treatment proved inconvenient because of the high instability of 30 percent H_2O_2; no ERC results were measured.

   Six percent dilutions of the stock H_2O_2 reagent were evaluated on another exhausted carbon cylinder. It was observed, however, that the 6 percent H_2O_2 solution effervesced, which, in turn, indicated

instability. Because the 3 percent H_2O_2 solutions were known to be the most stable aqueous form of this oxidant, further investigations were performed with this concentration. It was noted during the application of H_2O_2 that oxygen gas was evolved but that 3 percent solutions caused less flow blockage due to this effervescence. Seventy-one percent recovery was realized on the first ERC whereas 47 percent recovery was found on the second ERC. The third ERC gave a 20 percent recovery. No adsorptive capacity was noted on the carbon sample when subjected to a fourth ERC. It is thought that oxidants will remove some organics selectively and leave others on the pores. This theory would account for the arithmetic reduction of adsorptive capacity of the 3 percent H_2O_2-treated carbon.

The results obtained during the evaluation of each oxidant are pictured in Figures 9 through 16. For comparison, the results obtained in the screening of chemical oxidants for regeneration of tertiary-waste-exhausted, activated carbon are compiled in Table 4.

Table 4. OXIDANT REGENERATION EFFICIENCIES ON WASTE-EXHAUSTED, ACTIVATED CARBON, CLIFFS DOW, 10 × 30 MESH

Oxidant	Oxidant concentration, %	Average efficiency, %		
		First ERC	Second ERC	Third ERC
Chlorine water	0.46	15	0	
Bromine water	3.50	< 10	0	
$KMnO_4$	10.0	16	0	
$Na_2Cr_2O_7$	10.0	61	<20	
$K_2S_2O_8$	0.75	49	20	0
$Na_2S_2O_8$	0.75	55	<20	0
O_3	4.0	25	0	
Na_2O_2	1.0	60	<20	0
H_2O_2	3.0	71	50	<20

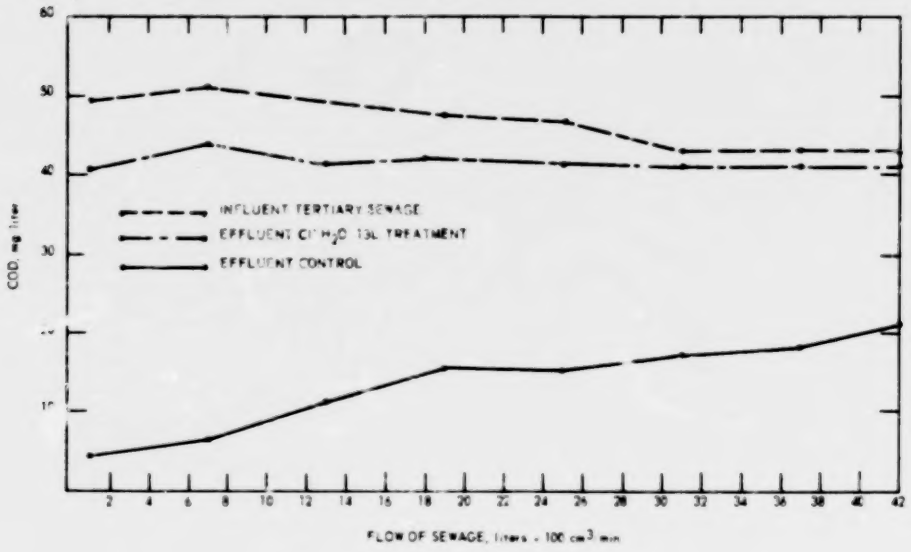
60
50
40
30
COD, mg liter
INFLUENT TERTIARY SEWAGE
EFFLUENT Cl H_2O TSL TREATMENT
EFFLUENT CONTROL
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40 42
FLOW OF SEWAGE, liters × 100 cm3 min

Figure 9. Percent recovery chlorine water, 50.0 g, Cliffs Dow, 10 x 30 mesh, 15% average efficiency.

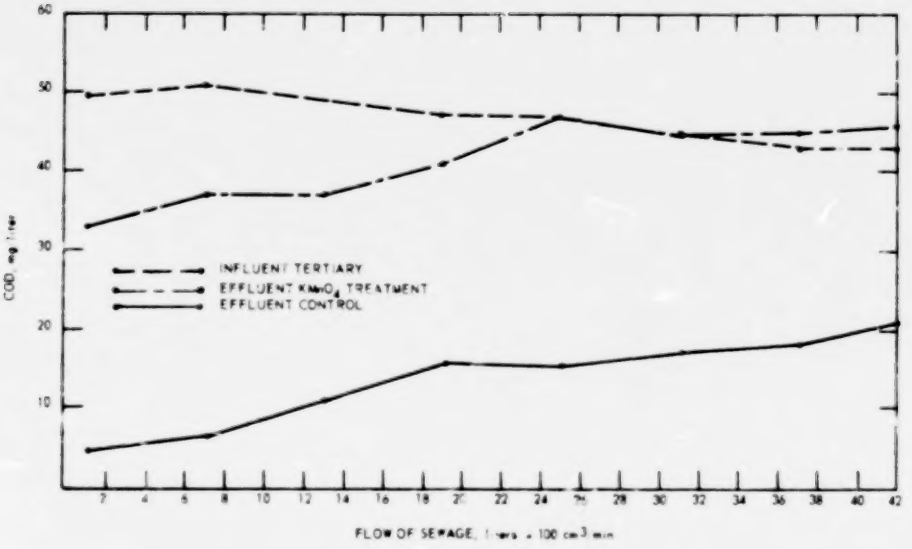

Figure 10. Percent recovery of $KMnO_4$, 6 liters, 50.0 g, Cliffs Dow, 10 x 30 mesh, 16% average efficiency.

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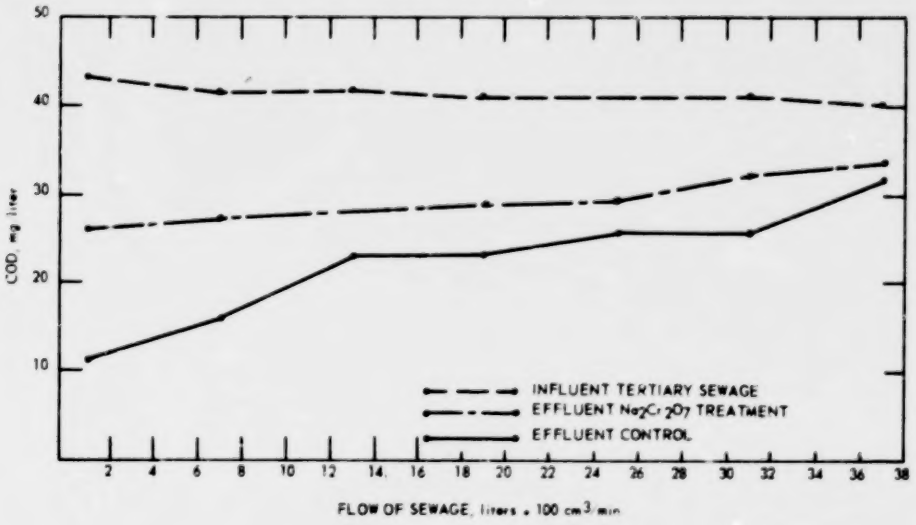

Figure 11. Percent recovery $Na_2Cr_2O_7$, 50.0 g, Cliffs Dow, 10 x 30 mesh, 60% average efficiency.

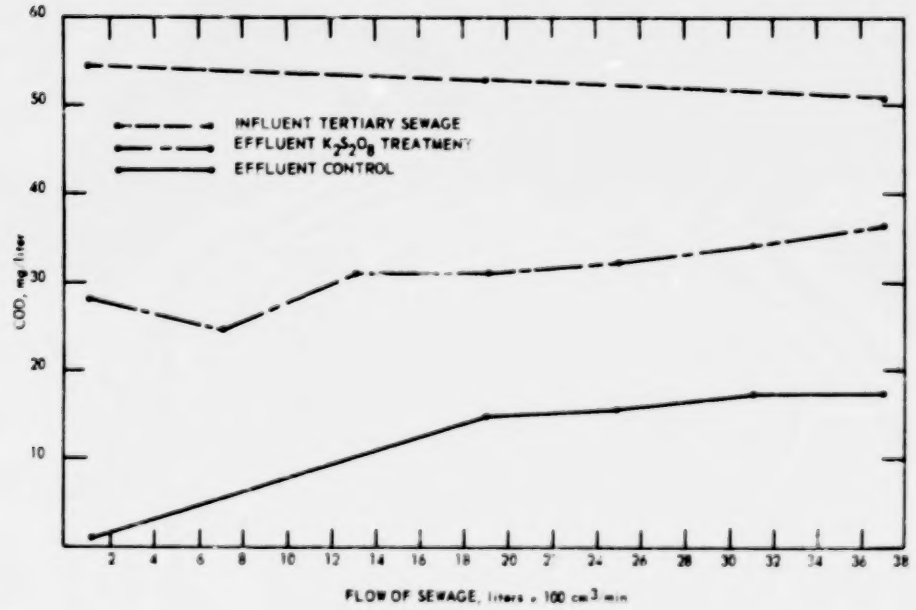

Figure 12. Percent recovery $K_2S_2O_8$, 50.0 g, Cliffs Dow, 10 x 30 mesh, 49% average efficiency.

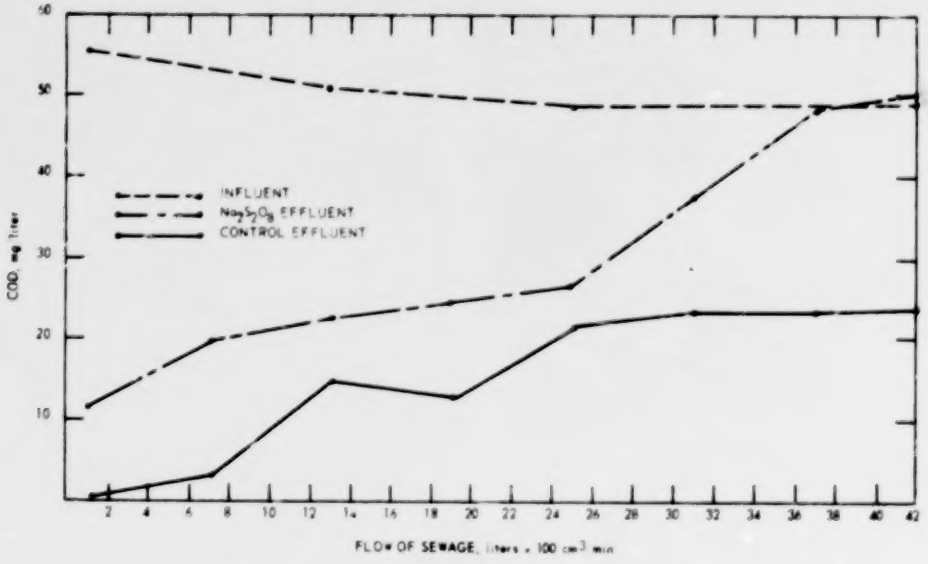

Figure 13. Percent recovery $Na_2S_2O_8$, 50.0 g, Cliffs Dow, 10 x 30 mesh, 55% average efficiency.

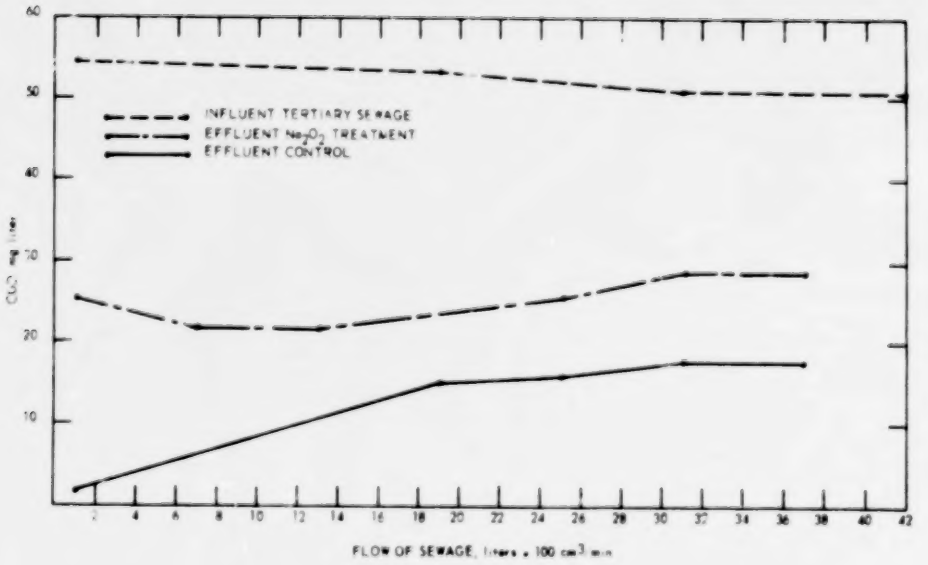

Figure 14. Percent recovery Na_2O_2, 1%, 50.0 g, Cliffs Dow, 10 x 30 mesh, activated carbon, 60% average efficiency.

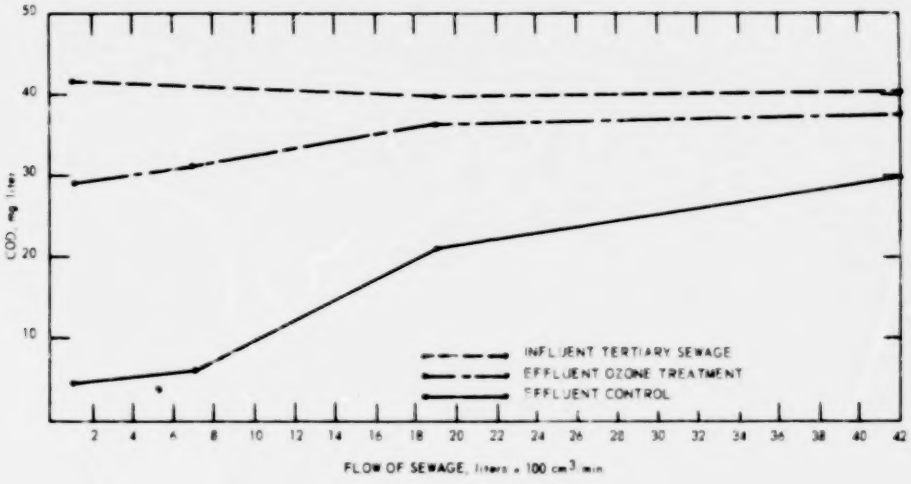

Figure 15. Percent recovery ozone, 50.0 g, Cliffs Dow, 10 x 30 mesh, 25% average efficiency.

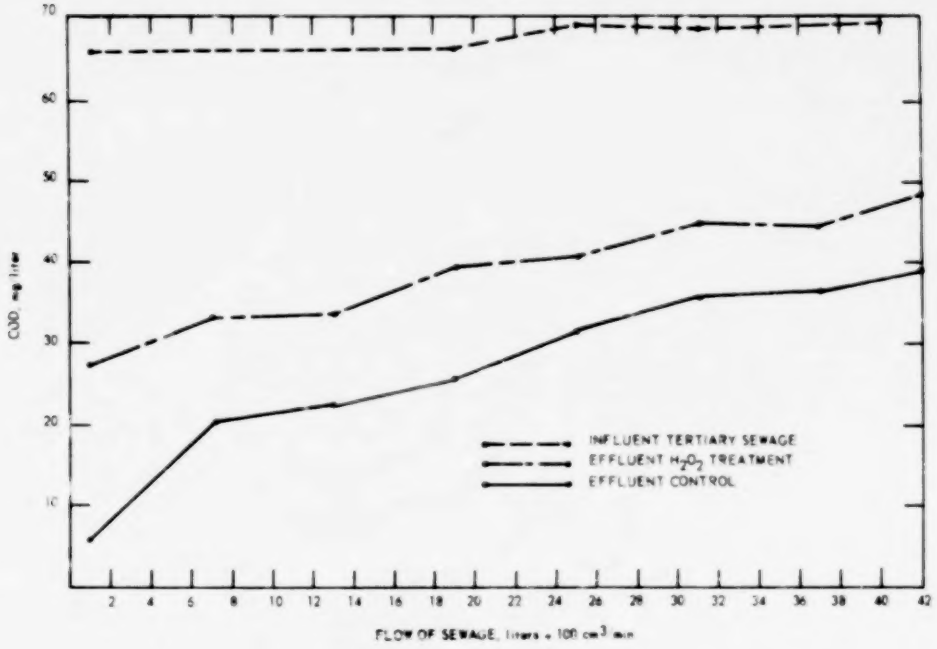

Figure 16. Percent recovery of 3% H_2O_2, 2 liters, Cliffs Dow, 10 x 30 mesh, activated carbon; phase 2 about 20° C, 70% average efficiency.

Discussion

None of the evaluated chemical oxidants achieved complete regeneration of the Cliffs Dow activated carbon that had been exhausted by tertiary waste water from Midland, Michigan, municipal waste water, under the experimental conditions used during this investigation.

This inability to regenerate the active carbon completely to its original state could arise from any of a number of causes that were not investigated. Some of the phenomena that could contribute to the incomplete regeneration of the active carbon are: Site poisoning, reaction rate with the contaminant, the blocking of micropores either by gas or oxidation products, diffusion of oxidant or product, degradation of active sites by oxidant, or reaction kinetics.

Still other factors could affect any comparative efforts to select the most effective chemical oxidant of those evaluated. For example, the effect of temperature, oxidant concentration, and time of exposure of the carbon to the oxidant could alter the apparent superiority of one candidate oxidant over another.

The results obtained in this phase of the investigation indicate, therefore, only that hydrogen peroxide appeared to be superior to any of the other chemical oxidants in the screening method used. The apparent superiority of hydrogen peroxide seems to be supported by the 47 percent regenerative efficiency on the second ERC. Furthermore, hydrogen peroxide was the only evaluated oxidant that provided a measurable regenerative efficiency on the third ERC.

None of the chemical oxidants screened was totally ineffective, as indicated by the percentile restoration of carbon adsorptive capacity on the first ERC. Distilled water was found to induce some percentage of recovery but only below 5 percent. All the oxidants gave higher percentile degrees than this.

Oxides of metals, represented by $KMnO_4$ and $Na_2Cr_2O_7$, did not appear to be satisfactory regenerants for the exhausted carbon. The dichromate demonstrated good regeneration, 60 percent on the first ERC, but dropped off considerably on the second. The permanganate presented an even poorer regenerative picture. Metallic ion residues, accumulating during the use of either of these two chemicals, could also pose a disposal problem.

Neither halogen, chlorine, or bromine was sufficiently effective for further consideration as a regenerant. The two persulfates, $K_2S_2O_8$ and $Na_2S_2O_8$, provided a surprising degree of regeneration on the first ERC. Here again, however, residues of the sulfates would occur in the effluent during the use and present an additional problem. Second ERC calculations, moreover, demonstrated that these persulfates were incapable of regenerating more than 20 percent.

The selection of hydrogen peroxide, then, as the best oxidant of those screened was based on: (1) The best regeneration obtained on the second ERC, and (2) the lack of residual problems.

PHASE 3.

ADDITIONAL HYDROGEN PEROXIDE STUDIES

Hydrogen peroxide appeared to be the most favorable oxidative regenerant for exhausted carbon as based on the previous investigations. During the contract time remaining, it was desirable to try to determine some of the optimum conditions for the use of hydrogen peroxide as an exhausted carbon regenerant. Experiments were also conducted to determine if ABS in tertiary-treated waste water could be adsorbed on activated carbon and if the carbon's capacity for this material could be restored with H_2O_2.

Experimental Procedures

MATERIALS AND EQUIPMENT

The previous evaluations of H_2O_2 as a regenerant for waste-exhausted carbon were conducted only at ambient temperatures. To consider the effect of an elevated temperature on the H_2O_2 efficiency, the apparatus shown in Figure 17 was used.

The same apparatus was used to determine the minimal volume of H_2O_2 solution necessary for the regeneration of exhausted carbon.

The materials necessary for ABS analyses were taken from Standard Methods, Eleventh Edition, page 246. The analysis required a Beckman Model B Spectrophotometer at a wave length setting of 650 microns.

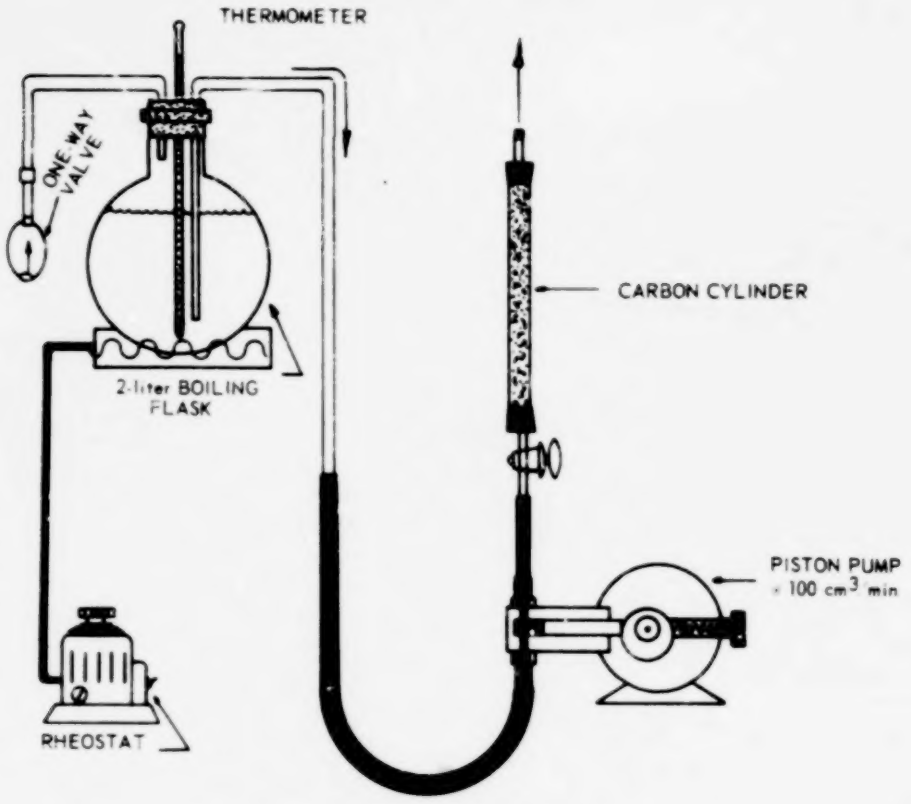

Figure 17. Elevated temperature apparatus, 60° C, 3% solution, H_2O_2 application.

METHODS

Hydrogen peroxide solutions with concentrations as great as 35 percent can be obtained commercially. The stock H_2O_2 solution used in the experiments was a 30 percent solution produced by Merck and Company.

It was advisable to try to find the smallest concentration of H_2O_2 that would provide satisfactory regeneration of waste-exhausted carbon. Dilutions of hydrogen peroxide were prepared down to a 1 percent concentration.

Comparative regeneration data were compiled for each of these concentrations. Moreover, the volume of carbon was varied at a constant 3 percent concentration of hydrogen peroxide.

Only two temperatures were compared for effect on hydrogen peroxide's regenerative abilities. An elevated temperature of 60°C was selected; results at this temperature were compared with those obtained at 20°C. The hydrogen peroxide concentration (3%) and volume (2 liters) were identical for both temperature evaluations.

Results

Determination of limiting concentration and solution volume of hydrogen peroxide for regeneration of waste-exhausted carbon* is summarized in Table 5.

Table 5. PERCENT EFFICIENCY OF HYDROGEN PEROXIDE FOR REGENERATION OF WASTE-EXHAUSTED CARBON

H_2O_2 solution concentration, %	Volume used, liter	Temperature, °C	Efficiency 1st cycle, %
30	2	20	No results
6	2	20	69
4	2	20	69
3	2	20	71
3	2	60	54
3	1	20	72
3	0.5	20	79
3	0.25	20	71
2	2	20	70
1	2	20	68

Analyses were made at various times throughout 1961 for total apparent ABS in Midland waste treatment waters. The results of this monitoring are listed in Table 6.

* Calculations of the efficiency percentage were identical to the method utilized for evaluation of the various oxidants in Phase 2.

The soluble surfactants in Midland waste waters caused slight foaming on the head of the pilot plant aeration tank. No foam difficulties were encountered owing to the rapid natural breakdown of the foam produced.

Table 6. ALKYLBENZENESULFONATE ANALYSES (DAILY FOR 1 WEEK)

Date	Total apparent ABS, mg/liter
2/9/61	2.96
2/10/61	2.80
2/11/61	3.04
2/12/61	2.48
2/13/61	3.04
2/14/61	3.24
2/15/61	2.86
Random samples	
10/6/61	2.20
12/1/61	2.00
12/5/61	2.50

Analyses for ABS were done on the three treatment effluents to determine if treatment degradation of surfactants occurred (Table 7).

Table 7. ABS ANALYSES OF THREE TREATMENT EFFLUENTS

Date	Midland plant primary treatment	ABS, mg/liter
10/6/61 10:00 AM	Effluent	2.0
10/6/61	Secondary pilot plant effluent	2.10
10/4/61	Composite sample of collected waste	2.40

An experiment was designed to determine if Cliffs Dow 10 x 30-mesh, activated carbon would adsorb ABS from waste waters. Thirty-seven liters of Midland, Michigan, tertiary waste water were pumped through 50-gram samples of Cliffs Dow activated carbon. Samples of 1-liter volume were taken of the tertiary waste water as well as of the carbon effluent. These samples were tested for milligrams of ABS per liter by the aforementioned methods. Results of ABS analyses during an ERC are recorded in Tables 8 and 9.

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Table 8. ABS ANALYSES, DECEMBER 1, 1961

Sample	COD, mg/liter	Throughput, liters	ABS, mg/liter	
8:00 a.m. tertiary-waste-water inf	41.1	1	1.55	
12:00 Noon tertiary-waste-water inf	41.0	19	1.95	Avg -
3:00 p.m. tertiary-waste-water inf	43.1	37	2.00	1.83 mg/liter
Effluent from carbon column				
1st liter, 100 cm^3/min	3.3		0.06	
13th liter, 100 cm^3/min	9.7		0.20	
25th liter, 100 cm^3/min	11.1		0.7	
43d liter, 100 cm^3/min	17.2		0.7	

Table 9. COD AND ABS ANALYSES, DECEMBER 5, 1961 (AFTER REGENERATION WITH 1% HYDROGEN PEROXIDE, 2 LITERS VOLUME)

Sample	COD, mg/liter	ABS, mg/liter
9:00 a.m. tertiary inf	39.7	2.05
12:00 Noon tertiary inf	40.0	2.51
3:00 p.m. tertiary inf	37.9	2.51
1st liter effluent	19.3	0.00
13th liter effluent	23.6	0.30
25th liter effluent	26.4	0.70
43d liter effluent	28.2	0.70

Discussion

The accumulated data from this supplementary hydrogen peroxide study were insufficient to determine specifically the exact volume, concentration, and temperature of hydrogen peroxide that would provide maximum regeneration of exhausted carbon. For instance, the rates of oxidation generally double for each 7 percent increase in temperature. Our data do not, however, support this statement since a lower efficiency was obtained when the H_2O_2 solution was maintained at 60°C than when it was maintained at 20°C. This lower efficiency most likely resulted from the deterioration of H_2O_2 at the elevated temperature. We would expect that physical variations within these conditions would have considerable effect on the efficiency of hydrogen peroxide. The data listed tend to indicate this.

According to the results, activated carbon can adsorb ABS from a municipal waste water after conventional waste treatment. Furthermore, the data suggest that hydrogen peroxide can regenerate exhausted, activated carbon to the extent that more ABS can be removed from a waste-water stream. No evidence was obtained to show that ABS was removed from the exhausted carbon by hydrogen peroxide; this possibility does, however, exist.

GENERAL DISCUSSION OF TOTAL PROJECT PHASES

Literature studies indicated that many carbons and chars are prepared from almost any material that was at one time either carbohydrate or cellulosic. These carbons are prepared by many different methods of activation for specific purposes. The carbon types may be classified on the basis of adsorptivity of gas or liquids. Most of these materials show selective adsorption properties; for example, a carbon may effectively remove H_2O_2 from air, but it may be of no value in removing the same compound from aqueous solution.

In choosing one carbon for the extraction of a contaminant from a liquid, there is no theoretical basis for the choice other than that of screening the carbons for effectiveness. The results of initial investigations of the adsorptive capacities of activated-carbon types showed that refractory organic compounds in Midland, Michigan, effluent (primary plus small, fabricated, secondary unit) waters could be removed by several activated-carbon types. The treatment processes at Midland Waste-Water Treatment Plant plus the fabricated pilot plant treatment unit removed 97 percent of the original suspended solids from the raw waste water and lowered the COD by 70 percent. Most of the remaining organics could be removed by adsorption on activated-carbon beds.

The screening studies of activated carbon done under this contract indicate a maximum COD loading of about 0.14 gram COD per gram of carbon under the experimental conditions utilized. Considerable variation was, however, noted among the active carbons tested.

It was further found that the carbon selected for regeneration studies was reactivated in a declining manner; that is, restored activity was always less than that found on the previous regeneration. The declining regeneration is thought to be

partially attributable to the concentration of regenerant used in these studies as well as to temperatures and other experimental variables. The results of ERC studies of oxidants indicate that hydrogen peroxide solutions produce the best regenerative effects on Cliffs Dow carbon exhausted with Midland waste water. All oxidants tested had some regenerative abilities. A general screening program of oxidants showed that hydrogen peroxide had the most favorable over-all regenerative ability. The choice of hydrogen peroxide was made on this basis as well as for ease of application and ready availability.

To make an economic study on the feasibility of activated-carbon adsorption and chemical reactivation for advanced waste treatment, liberties must be taken with the project data. Provisional acceptance of the following statements must be given:

> Cliffs Dow activated carbon gave the best adsorption of COD. This carbon costs $0.15 per pound.
>
> Hydrogen peroxide was the best regenerant for activated carbon exhausted by tertiary waste water. This oxidant costs $0.53 per pound (based on January 1963 average price of 50% H_2O_2, $0.265 per pound, delivered).
>
> One part of H_2O_2 is required to regenerate 3.3 parts of carbon to 70 percent of the initial capacity.

By using the above figures, calculations can be made of the cost required to regenerate carbon by chemical oxidation. On a pound-for-pound basis, it would cost $0.53 to regenerate activated carbon costing $0.50. Obviously, these figures indicate that it would be cheaper to discard the exhausted carbon than to attempt to regenerate it by means of chemical oxidants. If further calculations are made on the basis of 70 percent oxidant efficiency and declining efficiencies with multiple loading and regeneration steps, the economics appear even more unfavorable.

It is apparent that this uneconomical aspect of chemical-oxidant regeneration of carbon for use in advanced waste treatment could be altered if cheaper carbon and a cheaper, more efficient chemical regenerant could be found.

CONCLUSIONS

1. Activated carbon removed refractory contaminants from a tertiary-treated, municipal waste water.

2. Chemical oxidants partially regenerated activated carbon that had been exhausted by exposure to sand-filtered secondary effluent.

3. On a comparative basis, hydrogen peroxide displayed the most favorable over-all regenerative ability of the oxidants evaluated.

4. Because of only partial regenerative ability demonstrated by chemical oxidants, the adsorptive capacities of activated carbon were eventually destroyed.

5. Alkylbenzenesulfonate was adsorbed by activated carbon from a sand-filtered, municipal-waste-water, secondary effluent.

6. The data accumulated in this project suggested that chemical-oxidant regeneration of activated carbon exhausted by tertiary-treated waste water is not economically feasible.

ECONOMIC CONSIDERATIONS

It has been determined that activated carbon can adsorb refractory contaminants from tertiary, municipal waste. Furthermore, the exhausted carbon can be regenerated by chemical oxidants. To make an economic study of the feasibility of the use of activated carbon in advanced waste treatment, however, more information must be accumulated.

Time limitations prevented a thorough research into the best and most economical carbon type for use in waste treatment. The carbon type, in turn, may have a significant influence on the ultimate selection of a regenerant.

The following economic guide lines have been compiled as a criterion for selection of a carbon and a regenerant for advanced waste treatment.

The cost of COD removal from waste effluents with activated carbon has been treated in this evaluation on a purely operating basis since the unit process may be of a number of different types, and capital requirements would vary widely depending on the unit process involved and volumes handled. No attempt has been made to evaluate the inorganic removal.

An equation was derived that gives the cost per pound of COD removal on the assumption of a constantly declining regeneration of the activated carbon. The following equation is the basis of this analysis:

$$\text{Cost} \simeq \frac{(\text{Cost of carbon}) + n\ (\text{Cost of regeneration})}{\sum_{n=0}^{n} (\text{Regeneration factor})^n\ (\text{Initial loading})} \qquad (3)$$

Wherein

Cost = the cost per pound of the total COD removal if the carbon was discarded after the nth regeneration.

Cost of carbon = the price per pound of the active carbon used in the COD removal.

Cost of regeneration = the cost of regenerating 1 pound of active carbon regardless of its capacity or recovery. Assume no loss of carbon during regeneration.

Regeneration factor = the fraction of initial adsorption recovery obtained at the first regeneration and assumed constant for succeeding regenerations.

Initial loading = weight of contaminant adsorbed on a unit weight of activated carbon.

n = an integer defining the number of times a particular carbon is regenerated.

An example of the use of this formula may be illustrated by assuming conditions given in Figure 20.

Cost of carbon = 10 cents per pound
Cost of regeneration = 1 cent per pound
80 percent declining regeneration
10 percent initial loading

Cost at nth regeneration =

$$\frac{(\text{Cost of carbon}) + n\,(\text{Cost of regeneration})}{\sum_{n=0}^{n} (\text{Regeneration factor})^{n}\,(\text{Initial loading})} \qquad (4)$$

$$\text{Cost at 4th regeneration} = \frac{(10 \text{ cents/lb}) + 4\,(1 \text{ cent/lb})}{(0.80)\qquad\qquad (0.1)}$$

$$= \frac{14 \text{ cents per pound}}{(0.80 + 0.8^{1} + 0.8^{2} + 0.8^{3} + 0.8^{4})\,(0.1)}$$

$$= \frac{14 \text{ cents/lb}}{0.336} \quad 41.5 \text{ cents/lb}$$

The cost for COD removal under these assumed conditions is thus seen to be 41.5 cents per pound for all of the COD removal from solution up to the 5th regeneration. The carbon is assumed to be reloaded after the 4th regeneration.

For an estimation of the costs of activated carbon two situations must be considered. The first is when a displacement regeneration occurs wherein only a fixed fraction of the active sites is reactivated by the specific regenerant, and the second is when a decreasing regeneration is encountered. Both types of reactivation have been noted in the literature. The marked difference between the case of site poisoning and declining regeneration is indicated in Figure 18 where the dotted lines indicate various levels of declining regeneration and the solid lines indicate a comparative degree of initial site poisoning. This analysis is made on the basis of a quantity of carbon that initially removed 100 pounds of COD and is meant to indicate only differences in the mode of regeneration.

In the case of site poisoning, the initial activity is decreased to some fixed lower value in the first few regenerations owing to the poisoning of one type of active site and its consequent inactivation for future adsorptions. These cases are often encountered in the removal of products from biochemical processes. The COD adsorption from waste-water effluents would probably act more like a case of declining regeneration because of the spectrum of components that would allow for a continuing poisoning as a function of use. The site-poisoning case would, however, constitute a minimum cost situation.

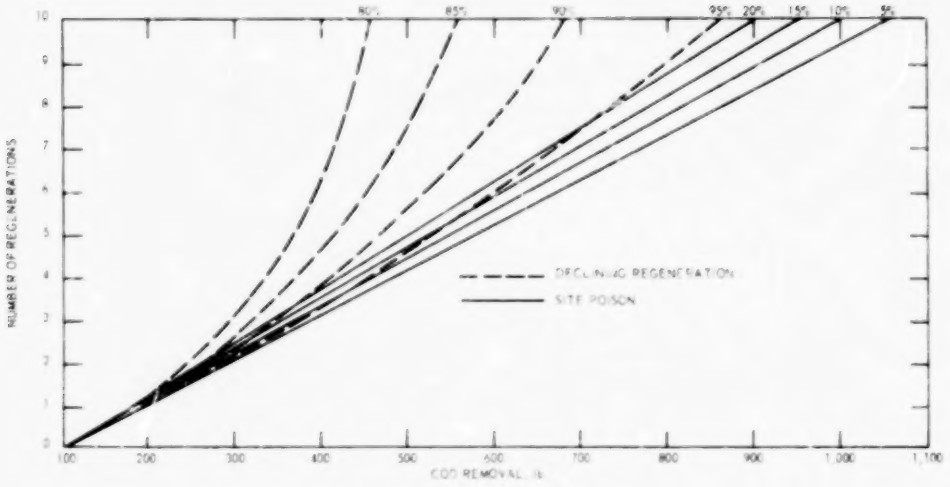

Figure 18. COD removal as a function of type of regeneration (assume initial carbon capacity of 100 lb COD).

Figure 19 indicates the cost per pound of COD removal (as COD) for six differently priced, activated carbons as a function of the number of regenerations for site poisoning.

Figures 20 through 24 indicate the relation of the cost of regeneration and the cost of activated carbon to the cost of COD removal for declining regeneration.

Circles in Figure 20 indicate where the cost of COD removal is minimum for each carbon cost. As the cost of carbon increases, the need for regeneration increases and the number of regenerations to obtain the minimum cost is increased.

A comparison between Figures 20 and 23 indicates the importance of high initial loading on the total cost of COD removal. It should be noted, however, that the number of regenerations required to obtain minimum cost depends upon the price of activated carbon and the cost of reactivation, and is independent of the initial loading.

Figure 24 shows the cost of COD removal by a 10-cent and a 30-cent carbon at three costs of regeneration and clearly indicates the importance of low-priced, activated carbons. From this figure it can be seen that a cheaper COD removal can be achieved when the 10-cent carbon is discarded after 2 regenerations at 5 cents per pound for each regeneration than is achieved with a 30-cent carbon after 10 regenerations at only 1 cent per pound.

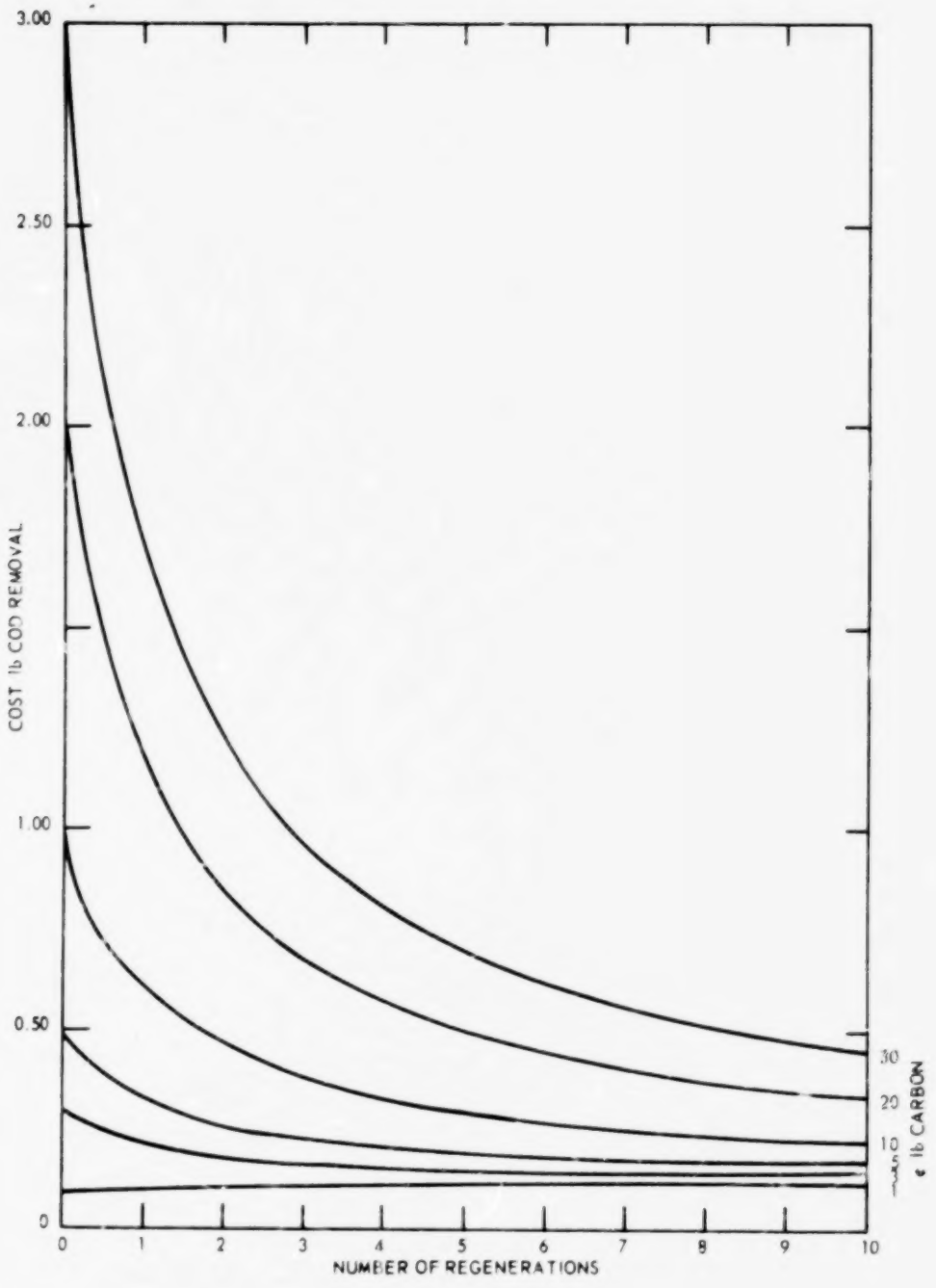

Figure 19. Effect of cost of carbon on COD removal (assume 10% initial COD loading, 20% poison, 1 cent/lb regeneration cost).

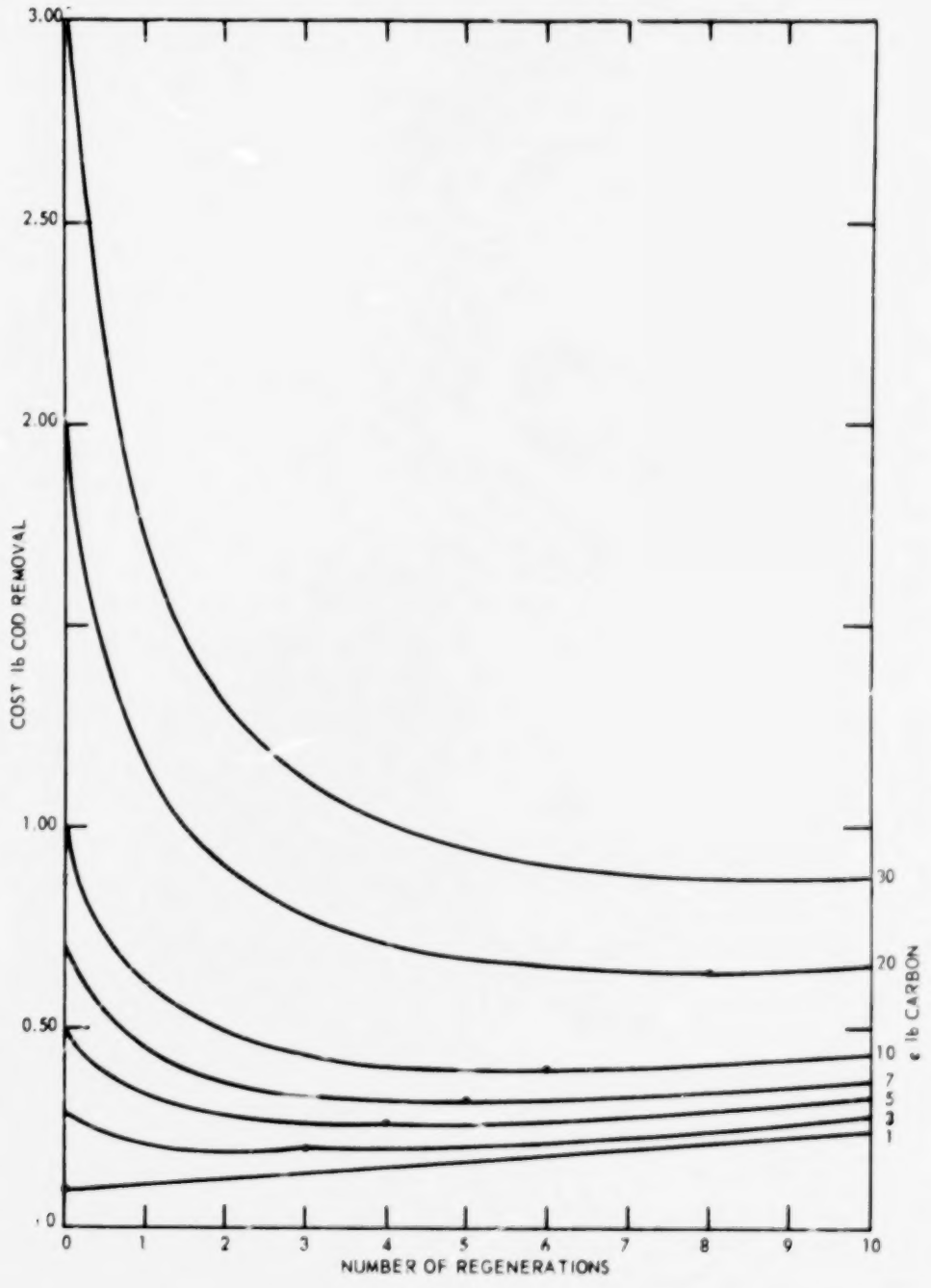

Figure 20. Effect of cost of regeneration on cost of COD removal (10% initial loading, 80% declining regeneration, 1 cent/lb regeneration cost).

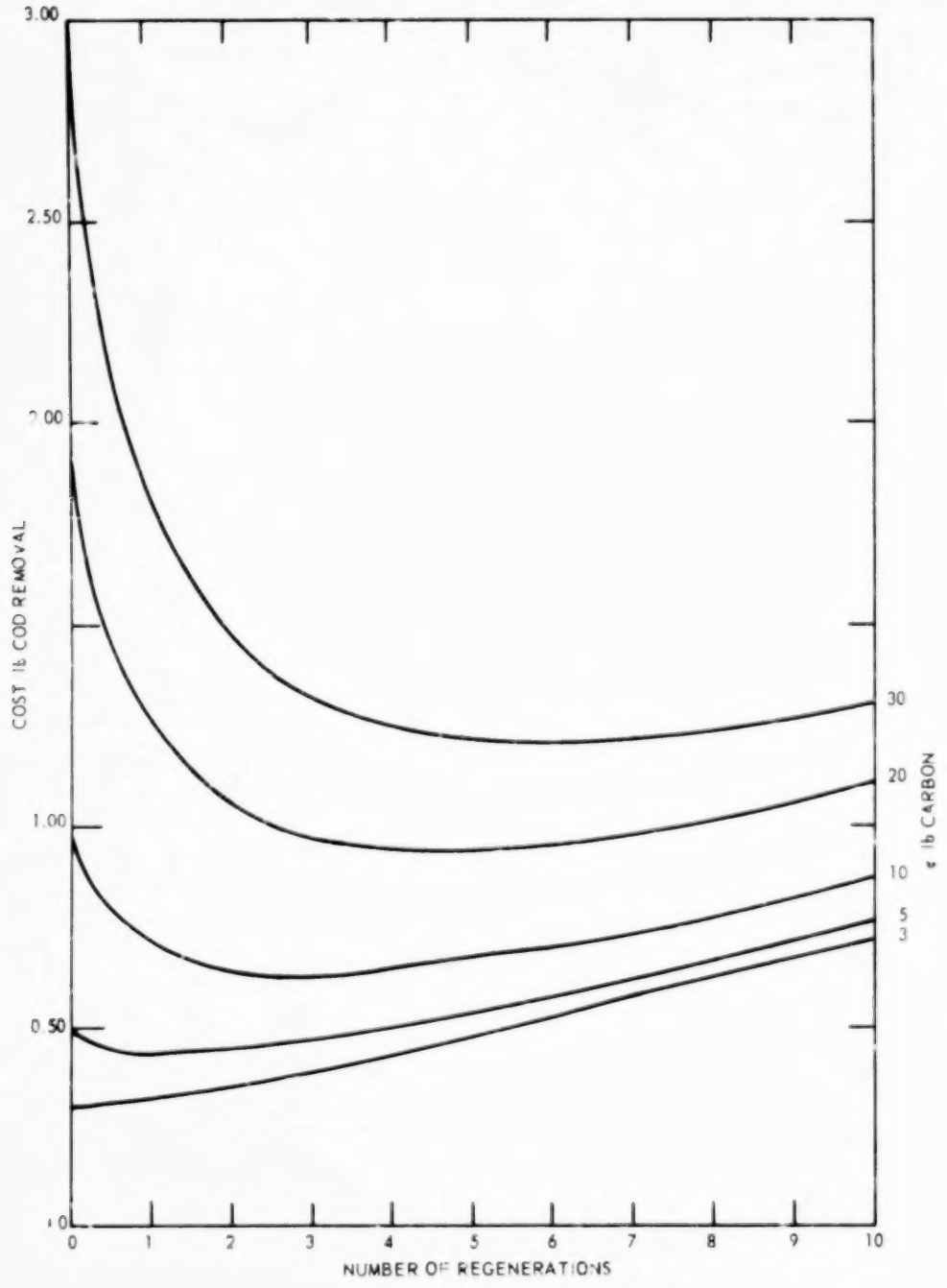

Figure 21. Effect of cost of regeneration on the cost of COD removal (10% loading, 80% declining regeneration, 3 cents/lb regeneration cost).

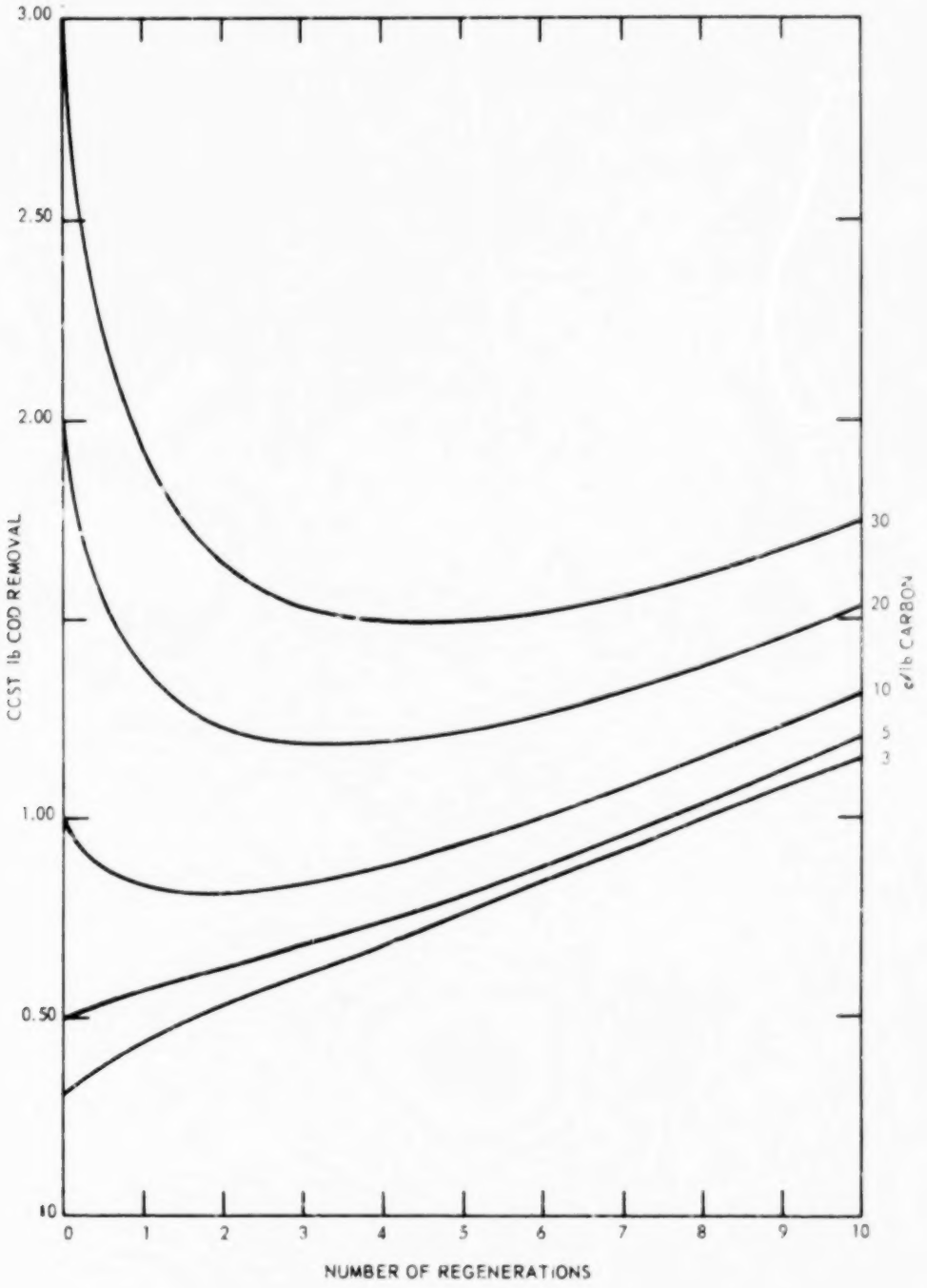

Figure 22. Effect of cost of regeneration on the cost of COD removal (10% loading, 80% declining regeneration, 5 cents/lb regeneration cost).

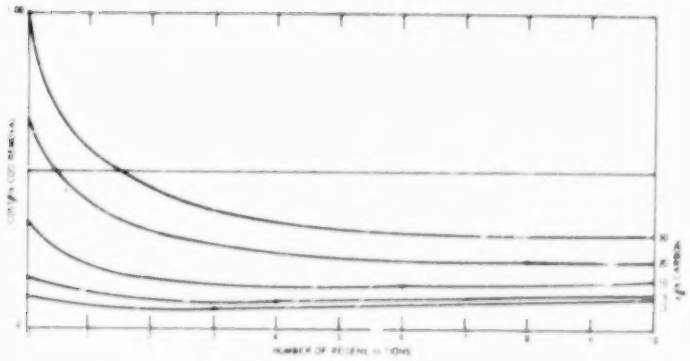

Figure 23. Effect of cost of carbon on COD removal at high initial loading (30% initial loading, 80% declining regeneration, 1 cent/lb regeneration cost).

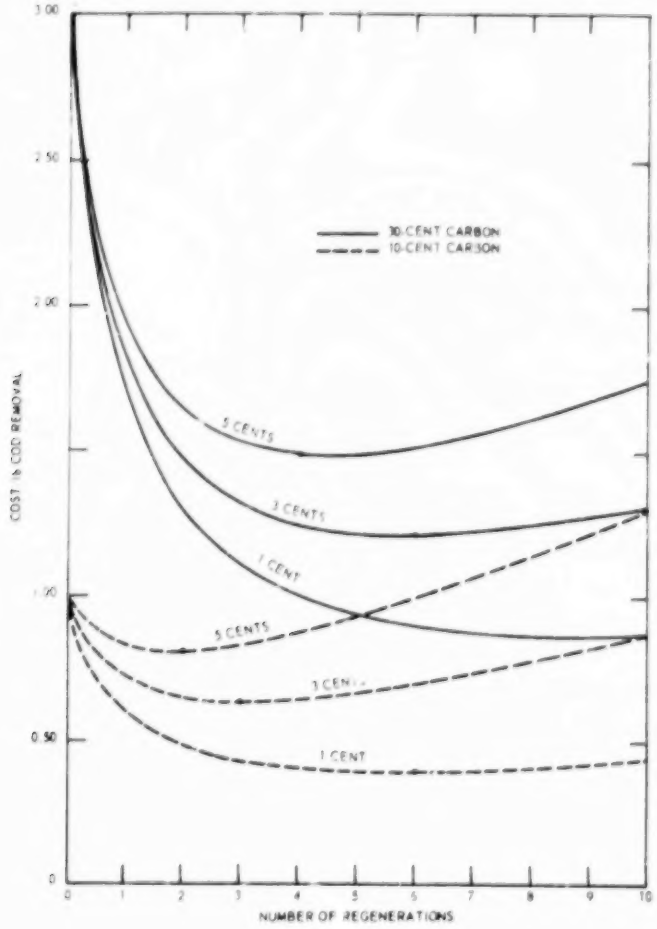

Figure 24. Effect of cost of regeneration on COD removal from 10-cent and 30-cent carbon (assume 10% initial loading, 80% declining regeneration and variable cost at regeneration).

REFERENCES

1. Amiot, R., Adsorption par le Charbon de Melanges Binaires in Solution Aqueous, Compt. rend, 199, 636-638, 1934.

2. A.W.W.A., Water Quality and Treatment, Second Edition, American Water Works Association, New York, 1951, pp. 233-234.

3. A.W.W.A., Water Quality and Treatment, Second Edition, American Water Works Association, New York, 1951, pp. 240-249.

4. Barry, H. M., Fixed-Bed Adsorption, Chemical Engineering, 67, 105-120, 1960.

5. Behrman, A. S., and Gustafson, H., Behavior of Oxidizing Agents with Activated Carbon, Industrial and Engineering Chemistry, 27, 426-429, 1935.

6. Berger, B. B., Public Health Aspects of Water Reuse for Potable Supply, Journal of the American Water Works Association, 52, 599-606, 1960.

7. Braus, H., Middleton, F. M., and Walton, G., A Study of the Concentration and Estimation of Organic Chemical Compounds in Raw and Filtered Surface Waters, Analytical Chemistry, 23, 1160-1164, 1951.

8. Brown, G. G., Unit Operations, John Wiley & Sons, Inc., New York, 1950, pp. 398-409.

9. Colebaugh, D., Filicky, J., and Hyndshaw, A., Factors Influencing the Efficiency of Activated Carbon, Journal of the American Water Works Association, 43, 322-326, 1951.

10. Culp, R. L., and Stoltenberg, H. A., Synthetic Detergent Pollution in Kansas, Journal of the American Water Works Association, 45, 1187-1195, 1953.

11. Deitz, V. R., United States Cane Sugar Refiners and Bone Char Manufacture and National Bureau of Standards, Bibliography of Solid Adsorbents, Washington, D.C., 1944.

12. Eckenfelder, W. W., Presentation as member of panel symposium on the Water Renovation and Desalination Program meeting of American Institute of Chemical Engineers, New York City, December 6, 1961.

13. Ettinger, M. B., Proposed Toxicity Screening Procedure for Use in Protecting Drinking Water Quality, Journal of the American Water Works Association, 687-694, 1960.

14. Freundlich, H., and Masius, M., Absorption in a Solution of Several Substances, van Bemmelen Gedenboek, 88-101, 1910.

15. Harrison, L. B., Activated Carbon at Bay City's Filtration Plant, Journal of the American Water Works Association, 1388-1392, 1931.

16. Harrison, L. B., Use of Granular Activated Carbon at Bay City, Journal of the American Water Works Association, 32, 593-608, 1940.

17. Hassler, J. W., The History of Taste and Odor Control, Journal of the American Water Works Association, 32, 2124-2152, 1941.

18. Hassler, J. W., Activated Carbon, Chemical Publishing Company, Inc., Brooklyn, New York, 1951.

19. Hurwitz, E., Beaudoin, R. E., Lothian, T., and Sniegowski, M., Assimilation of ABS by Activated Sludge Treatment Plant-Waterway System, Journal of the Water Pollution Control Federation, 32, 1111-1116, 1960.

20. Lieber, M., Syndet Removal from Drinking Water Using Activated Carbon, Water and Sewage Works, 107, 299-301, 1960.

21. Ludzack, F. J., Laboratory Model Activated Sludge Unit, Journal of the Water Pollution Control Federation, 32, 605-609, 1960.

22. Mantell, C. L., Chemical Engineers Handbook, Section 14, McGraw-Hill, New York, 1950.

23. McGauhey, P. H., and Klein, S. A., Removal of ABS by Sewage Treatment, Sewage and Industrial Wastes, 31, 877-899, 1959.

24. McKinney, R. E., and Donovan, E. J., Bacterial Degradation of ABS, II. Complete Mixing Activated Sludge, Sewage and Industrial Wastes, 31, 690-696, 1959.

25. McKinney, R. E., and Symons, J. M., Bacterial Degradation of ABS, I. Fundamental Biochemistry, Sewage and Industrial Wastes, 31, 690-696, 1959.

26. Middleton, F. M., Braus, H., and Ruchhoft, C. C., The Application of the Carbon Filter and Countercurrent Extraction to the Analysis of Organic Industrial Wastes, Proceedings of the 7th Purdue Industrial Waste Conference, Series No. 79, 439-454, 1952.

27. Middleton, F. M., and Lichtenberg, J. J., Measurement of Organic Contaminants in the Nations' Rivers, Industrial and Engineering Chemistry, 52, 99A-102A, 1960.

28. Middleton, F. M., Advanced Waste Treatment - A Challenge to the Community, Statement read as part of panel discussion on the Water Renovation and Desalination Program meeting of American Institute of Chemical Engineers, New York City, December 6, 1961.

29. Nellensteyn, F. J., De Activiteit van Grafiet en Diamant en de Modificaties der Amorphe Koolstof, Chemical Weekbald, 22, 291-293, 1925.

30. Ockrent, C., Selective Adsorption by Activated Charcoal from Solutions Containing Two Organic Acids, Journal of Chemical Society, 33, 613-130, 1932.

31. Renn, C., and Barada, M., Adsorption of ABS on Particulate Materials in Water, Sewage and Industrial Wastes, 31, 850-854, 1959.

32. Ruchhoft, C. C. Middleton, F. M., Braus, H., and Rosen, A., Taste and Odor Producing Compounds in Refinery Gravity Oil Separator Effluents, Industrial and Engineering Chemistry, 46, 284-289, 1954.

33. Ryckman, D. W., Burbank, N. C., and Edgerley, D., Methods of Characterizing Organic Materials of Taste and Odor Significance from Missouri River Waters, American Chemical Society Convention, September, 1959.

34. Sigworth, E. A., Activated Carbon - Its Value and Proper Points of Applications, Journal of the American Water Works Association, 29, 688-698, 1937.

35. Sipyagin, A. S., and Serkin, E. S., Regeneration of Activated Carbons, Zhur, Sakhur, Prom., 4, 176-181, C. A. 24, 6052, 1930.

36. Syverson, G., and Timmer, R., Laundering Spent Carbon for Reuse, Food Engineering, 32, 107-108, 1960.

37. Vaughn, J. C., and Falkenthal, R. E., Detergents in Water Supplies, Industrial and Engineering Chemistry, 48, 241-245, 1956.

38. Standard Methods for the Examination of Water and Waste Water, Eleventh Edition, American Public Health Assoc., Inc., New York, 1960.

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